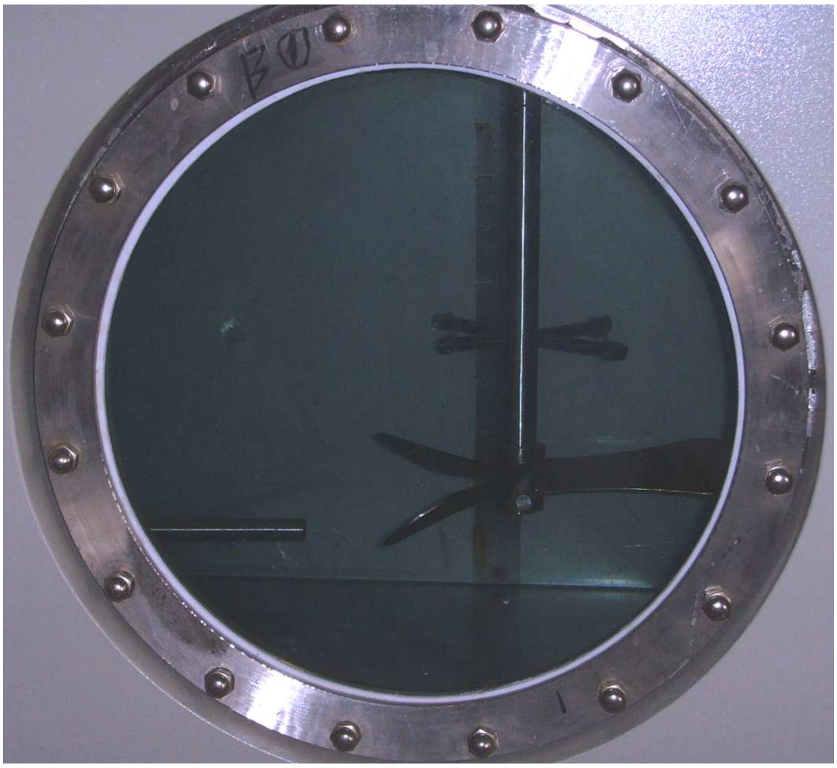
NCSEMC
North China Sea Environmental
Monitoring Center of State Oceanic
Administration, P.R. China.

Bonn -OSINET
Oil Spill Identification
Network of Experts
within the Bonn-Agreement

Round Robin 2010 –

The comparison of HFO and Crude Oil Samples

Fifth intercalibration in the framework of Bonn-OSInet
The results of 24 international laboratories



On the front page:

Internal structure of the marine environment simulating device.

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Fifth intercalibration in the framework of Bonn-OSInet
The results of 24 international laboratories

Colophon

Institute NCSEMC
North China Sea Environmental Monitoring Center
of State Oceanic Administration, PR. China.
22 Fushun Road, Qingdao, China

Information Zhou Qing
Email xxzhouqing@hotmail.com

Authors Zhou Qing and Sun Peiyan

Clients RR2010 participants
Bonn-OSInet expert group
Bonnagreement

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Contents

Executive summary

Round Robin 2010 was the fifth world-wide ring test of the expert group on oil spill identification of the Bonn-Agreement (Bonn-OSInet), in which 24 laboratories from 18 countries participated.

In this Round Robin test, the samples were prepared by The North China Sea Environmental Monitoring Center of State Oceanic Administration of P. R.,China. Five oil samples were sent to the participants. It was requested to work (if possible) according to the “final” version of CEN-TR 2v2, i.e. a version open for comments that have been published on the forum in August 2010. Participants were asked to send an internal-technical report by email (See 7.2 and Annex J of the draft version 38 of the CEN-TR). The original reports have been combined in a final report, together with an evaluation of the overall results.

The laboratories were requested to report the type of oil, with reasons, and to compare the spill samples (1, 2 and 3) with the candidate source samples (4 and 5).

Table 1. Participating laboratories

Laboratory	Location	Contact
EPA	Macleod (AU)	Syed Hasnain
NSWDECC	Lidcombe (AU)	Val Spilmans / Steve Fuller
SGS	Varna (BG)	Veselka Pashova / William Froude
PESCEC	Vancouver (CA)	Dayue Shang
ESTS	Ottawa (CA)	Chun Yang
EERC	Tallinn (EE)	Juhan Tamm
NBI	Vantaa (FI)	Niina Viitala
LASEM	Toulon (FR)	Jean Ulrich Mullot
CEDRE	Brest (FR)	Julien Guyomarch
LVGMC	Riga（LV）	Irina Dzene / Rita Skolmeistere
RWSWD	Lelystad (NL)	Paul Kienhuis
NFI	Den Haag (NL)	Rene de Bruyn
SINTEF	Trondheim (NO)	Liv-Guri Faksness / Per S. Daling
SKL	Linkoping (SE)	Magnus Källberg
CSIC	Barcelona (Spain)	Joan Albaiges
NewFields-EFP	Rockland (US)	Scott A. Stout
CEDEX	Madrid (Spain)	Ricardo Obispo
BSH	Hamburg (DE)	Gerhard Dahlmann
Petrobas	RiodeJaneiro (BR)	Fabiana D.C.Gallotta
ERT	Edinburgh (UK)	Gordon Todd
NCSEMC	Qingdao (CN)	ZhouQing / WangXinping
ISPRA	Rome（IT）	Giulia Romanelli / Marina Amici
BMM	Oostende (Be)	Marijke Neyts / Patrick Roose
ALET	Moncton (CA)	Josée Losier / Art Cook

The participating laboratories are listed in Table 1 while the results are summarized anonymously in Table 2. Each lab has been given a random number, that will be used throughout the whole text of this document.

Table 2. Comparison of Spill Oils and Source Oils

Participant	RR2010-1 with		RR2010-2 with		RR2010-3 with	
	RR2010-4	RR2010-5	RR2010-4	RR2010-5	RR2010-4	RR2010-5
1	NM	NM	PM	NM	PM	NM
2	NM	NM	M	NM	M	NM
3	NM	NM	M	NM	M	NM
4	NM	NM	M	NM	PM	NM
5	NM	NM	M	NM	M	NM
6	NM	NM	M	NM	M	NM
7	NM	NM	M	NM	M	NM
8	NM	NM	M	NM	M	NM
9	NM	NM	M	NM	M	NM
10	NM	NM	M	NM	PM	NM
11	NM	NM	M	NM	M	NM
12	NM	NM	M	NM	M	NM
13	NM	NM	M	NM	M	NM
14	NM	NM	M	NM	PM	NM
15	NM	NM	M	NM	PM	NM
16	NM	NM	M	NM	M	NM
17	NM	NM	M	NM	PM	NM
18	NM	NM	M	NM	I	NM
19	NM	NM	M	NM	M	NM
20	NM	NM	M	NM	M	NM
21	NM	NM	M	NM	M	NM
22	NM	NM	M	NM	M	NM
23	NM	NM	M	NM	M	NM
24	NM	NM	M	NM	PM	NM

The oil type of sample 1 seems to have a composition that partly points to HFO, but also to crude oil. The sample has been introduced to the Round Robin, because this type of oil is more often found by NCSEMC and is not described in the CEN/Tr.

Non of the participants seen this oil composition before, indicating that this type of oil probably is only used / produced in countries in the vicinity of the Bohai Sea.

The spill samples 2 and 3 were prepared from source sample 4. Source sample 5 is from a crude oil that is found in the same area as sample 4.

All participants were able to come to the right conclusions, although some were less certain, because of the heavy and complex weathering of spill sample 3.

1 Introduction

This report is the summary report of Round Robin 2010. The individual reports of the participants are available on the Bonn-OSInet forum (password protected). The summary report is publicly available on the Bonn-OSInet section of the Bonnagreement website (www.bonnagreement.org). For confidential reasons the results of the participants are indicated anonymously in the summery report; each lab has been given a random number, that will be used throughout the whole text of this document.

The method advised is the “final” version of CEN-TR 2v2, i.e. a version open for comments that have been published on the Bonn-OSInet forum in August 2010.

The summary report starts with the invitation letter (see Chapter 2) send to 24 laboratories listed in Table 1. The letter contains an introduction to the annual round robins in the framework of Bonn-OSInet, describes the scenario of the case and gives instructions how to handle the samples and send in the analysis report.

Results received from the laboratories are listed in Table 2. In this table, 3 spill samples were compared to 2 source samples. The results of identification of the oil type are listed in Table 5.

2 Instructions

On 15-8-2010 the instructions for RR2010 were published on the Bonn-OSINET forum:

Subject

Oil Spill Identification Round Robin 2010

Dear Colleagues,

This is the fifth oil spill identification intercalibration round within the Bonn-OSINET expert group.

We have prepared five samples for comparison.

Scenario and sample information:

In June of 2010, some spill oil was found in the north coastal area of the Bohai Sea. Two spill samples were sent to our centre by a local monitoring station, one from a harbour and another from a beach. The sample from the harbour is indicated with RR2010-1, and the sample from the beach is indicated with RR2010-2. One month later, another spill sample was taken in the same beach area, indicated with RR2010-3.

Two suspected source samples were taken from an oil pipeline terminal nearby. The samples were taken from two main pipelines connected to different platforms. The suspected source samples are indicated with RR2010-4 and RR2010-5.

To be able to send all participants the same samples, the oil spill samples have been dissolved in DCM at a concentration of 100 mg/ml.

Method

The method advised is the "final" version of CEN-TR 2v2, i.e. a version open for comments that have been published on the forum in August.

Reporting

We like to ask you to analyse and compare the spill samples of RR2010-1 RR2010-2and RR2010-3, identify the oil type (crude oil or fuel oil? or some other type? explain the reasons), and compare the spill samples with the 2 suspected source samples RR2010-4 and RR2010-5.

Send an internal-technical report by email (See 7.2 and Annex J of the "final" version of the CEN-TR). The original reports will be combined in a final report, together with an evaluation of the overall results.

According to the CEN-TR, you have to produce and compare ratios and plots, and to use these means in your reports.

The spreadsheet provided the last years may be of great help here. Paul have put an improved version of this spreadsheet on our server.

Time schedule

15-8-2010:	*The samples have been sent out.*
Before 1 November:	*Reports have been returned.*
December:	*Final report will be sent to the participants.*

Meeting:

Send the results by email to: xxzhouqing@hotmail.com, and Gerhard.dahlmann@bsh.de.

Yours sincerely,
Sun Peiyan
Zhou Qing
Paul Kienhuis, RWS-WD.
Gerhard Dahlmann, BSH.

3 Real scenario

The North China Sea Environmental Monitoring Center of State Oceanic Administration of P. R.China（NCSEMC, Qingdao）joined with the Key Laboratory of Marine Spill Oil Identification and Damage Assessment Technology, SOA, and is responsible for:

- marine environmental monitoring, investigation, and assessment in Chinese northern maritime territories (the northern part of the Yellow Sea and Bohai Sea),
- the environmental protection connected with marine oil exploitation activities and
- the assessment on oil spill accidents in its administrative areas.

The Bohai Sea is one of the most important areas for oil exploitation and oil transport in China. Every year, some oil spills happen in the Bohai Sea, of which more than 70% are mystery spills. Our duty is, first to tell the oil type (crude oil or fuel oil) of the mysterious spill.

In case of a fuel oil, the MSA(Maritime safety Administration of P.R.China) and other departments are responsible to find out which vessels caused the spill. In case of a crude oil, we must tell whether it comes from Bohai Sea oil field, and which oil platform caused the spill.

This year we have the honor to prepare the Round Robin Test, we hope to “share” our problems with colleagues in this family. In this way, we can learn and improve together. The problems included in this Round Robin Test, are mixing or a special type of HFO, similar crude oil, evaporation and biodegradation.

3.1 RR2010-1 sample

RR2010-1 sample is a mystery spill oil sample from the Bohai Sea that we received on May 2, 2010. Since 2008, this type of mineral oil was often found in Bohai Sea. We identified it as HFO, but the extremely high retene confused us a lot: is it a kind of special fuel oil, or is it a mixture of fuel oil and crude oil? Where did it come from, we haven’t find any crude oil in our database (we have about 1500 oil samples in our database, mostly from marine oil field of China, also some imported crude oil samples and fuel oil samples) which has so high retene concentration. Does the retene come from the crude oil which did not crack during the refining process, or does it come from mixing, or contaminants? We have a limited knowledge about crude oils from other areas, and don’t know any special contaminants containing retene. So, we choose this mysterious spill sample as RR2010-1. Let all colleagues study it. In chapter 5, we will describe more about the characters of this kind of mysterious spill oil.

3.2 RR2010-2, RR2010-3, RR2010-4 samples

RR2010-2，RR2010-3，RR2010-4 are designed for the problems of evaporation, biodegradation and water washing. Although they have been well studied and most colleagues of this group are quite familiar with the fingerprinting change, for the serious biodegradation spill samples, we still felt difficult to determine whether the degradation happened after the spillage in the environment, or happened underground before the spill. This is based on our experience with an oilfield in the Bohai Sea that exploits crude oil from layers on different depths. The degree of biodegradation of the crude oil is gradually changing from layer to layer.

In 2006, this oilfield had a pipeline leakage. One month later, oil was fetched on a beach nearby. The spill sample showed a serious biodegradation compared to the oil from the leakage. We concluded a “probable match” according to the “final” version of the CEN-TR:

when differences in chromatographic patterns and diagnostic ratios of the samples submitted for comparison are lower than the variability of the method or can be explained unequivocally, for example by weathering. The samples are considered to be identical beyond any reasonable doubt.

Serious biodegradation could be explained, but we don’t think it is unequivocally. We think that this problem should be studied more.

3.2.1 Preparation of the biodegradated samples

In 2009 we had a research project on spill oil bioremediation with Ocean university of China, Nankai Univerisity and other departments. We conducted the lab experiments and field experiments. The samples RR2010-2, RR2010-3 and RR2010-4 were chosen from the lab experiments. We will introduce the two parts of these experiments shortly. The results of this research will be published in the future.

3.2.2 Lab research.

- Hydrocarbon degrading bacteria screening

Hydrocarbon degrading bacteria (N1, N2, N3, and N4) and biosurfactant producing bacterium B-1 were selected to prepare for the bioremediation experiment, which were screened from petroleum contaminated seawater of the port of Qingdao.

The information about the bacteria applied are listed in Table 3.

Table 3. Bacteria used for the experiments.

Strain	Genbank accession number
Ochrobactrum N1	HQ231209
Brevibacillus parabrevis N2	HQ231210
Brevibacillus parabrevis N3	HQ231211
Brevibacillus parabrevis N4	HQ231212
Brevibacillus parabrevis B-1	HQ231213

- Marine environment simulating device design

The marine environment simulating device was special designed for this research. The internal tank size was 1.5 m (L) ×0.8 m (W) ×0.7 m (H). It could be filled up with 840 L water. The device, equipped with refrigeration and heating equipment, could maintain a steady temperature. It had an aerator and a stirrer under water, as shown in Fig.1, so that the dissolved oxygen (DO) could be kept at a certain level. Data of temperature, pH and DO were recorded every minute by the upper computer automatically.

Fig.1. The marine environment simulating device.

- Experiment process

This experiment was conducted in the underground chamber of our department. Two bioremediation experiment chamber devices were used. One was the control and the other was the experimental. Each tank was added 720L artificial seawater and spread with 600 ml crude oil. The bioremediation experiment was carried out at 25°C for 10 days. During these days, the room temperature was about 19°C. Both tanks were aerated and stirred at regular intervals. Floating oil samples were tested everyday over a period of 10 days. In order to investigate the oil-degrading ability of N-series bacteria consortium without human interventions, the bioremediation experiment was conducted under natural conditions for about 4 months after the 10 days' regular investigation. Floating oil was sampled from the water surface using a five-point method and analyzed till the 144 d. The room temperature fluctuated slightly around 0°C.

∗ Artificial seawater: It included 3.75% (w/v) NaCl, 11.67% (w/v) MgSO4·7H2O and 0.06% (w/v) NaHCO3.

∗ Crude oil: It was sampled from a reservoir of the Bohai oilfield (viscosity 22.2mPa·s (50°C, 50 rpm), density 0.8552 g·cm3).

We chose the original tested crude oil as RR2010-4. RR2010-2 was a light weathered sample, fetched at the 10th day. RR2010-3 was a serious weathered sample, fetched at the end of the experiment on the 144th day.

3.2.3 Field experiment

We built several ponds near a coastal beach. The area of each pond is 4m*4m. The experiment period is from 11 July to 27 October (103 days). The water depth is about 70cm. Different hydrocarbon degrading bacteria groups were put into these ponds according to the quantity of 3 L/m^2. The crude oil was put into pond with a quantity 1 L/m^2, so 16 L/pond. Samples were taken on the 3rd, 11th, 19th, 33rd, 66th and 103rd day. During these days, the temperature was 10-38 ℃ and it rained frequently the first 50 days.

Fig.2. Bioremediation Field Experiment.

3.3 RR2010-5 sample

This sample was intended to represent a different crude oil with properties very close to the crude oil used for the experiments. In the Bohai Sea oilfield, some platforms produce almost the same crude oil. In one spill case, we sampled 20 suspicious platforms, but with the analysis technique and identification indices we use nowadays they could not be distinguished. The results of the round robin test showed however, that RR2010-5 has not been selected successfully. The distinct difference between RR2010-5 and RR2010-4 made all participants to conclude a non-match without any difficulty.

4 GC-FID Evaluation

According to version 38 of CEN-TR 2v2, the chemical fingerprinting analysis in the laboratory starts with the GC-FID screening. The data from this screening should be used for:

- characterizing the oil sample(s) by obtaining the overall boiling (carbon) range of the oils, i.e., the total distribution of hydrocarbons including n-alkanes from C10 to C40 if present. For an overview of boiling points of n-alkanes;
- visual inspections of the chromatograms for possible characteristic features and a tentative classification to a type of the spilled oil and source oils if possible;
- determining the degree of weathering;
- establishing selected acyclic isoprenoid ratios (C17/pristane; C18/phytane and pristane/phytane).
- eliminating samples for the GC-MS analysis (level 2) if they are obvious “non-matches” to the spilled oil
- adjusting the injection concentration of the samples to mid-level for the GC-MS analysis.

The GC-FID chromatograms of the RR2010 samples are show in Fig. 3 to Fig. 7.

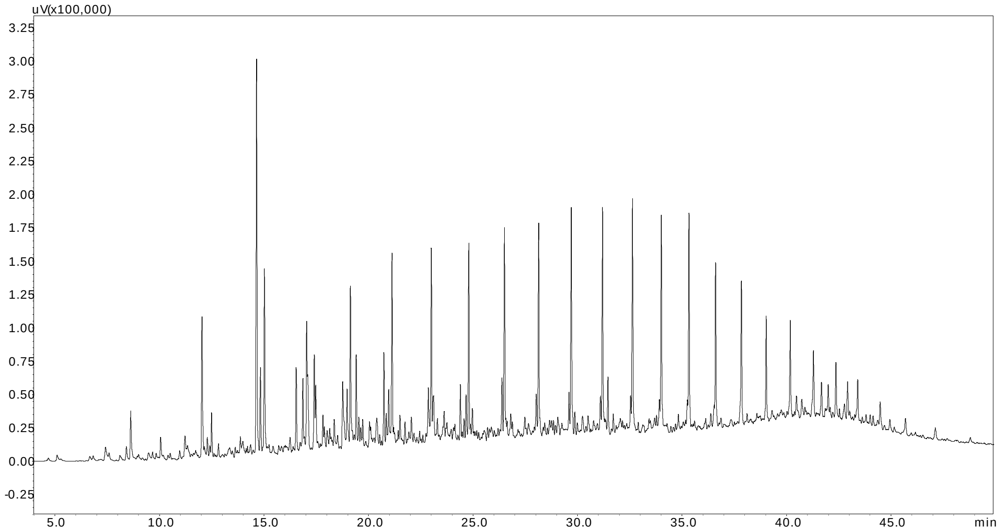

Fig.3. Spill sample from harbour, RR2010-1.

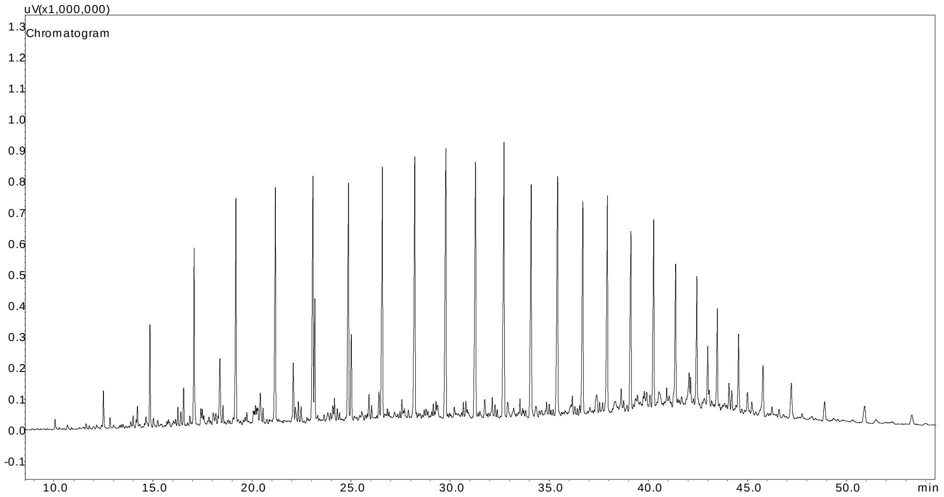

Fig.4. Spill sample from beach, RR2010-2.

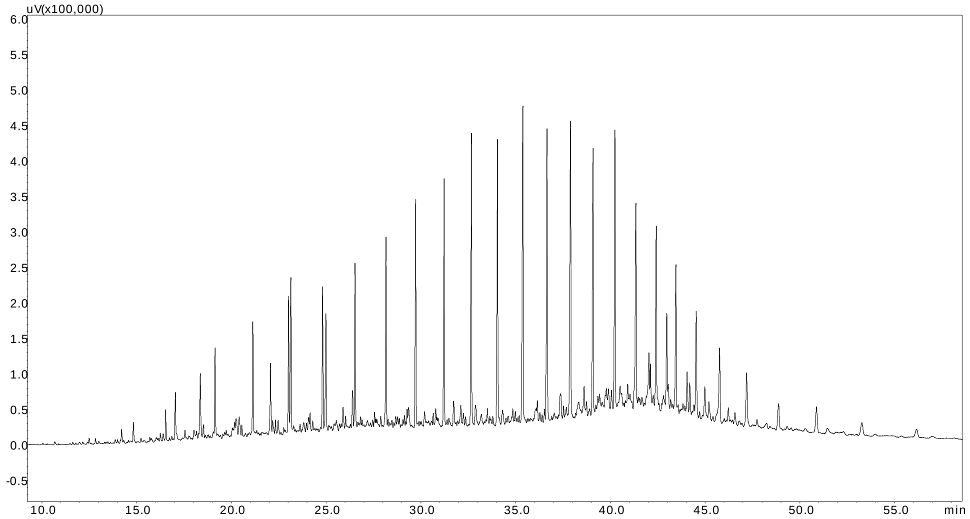

Fig.5. Spill sample from beach, RR2010-3.

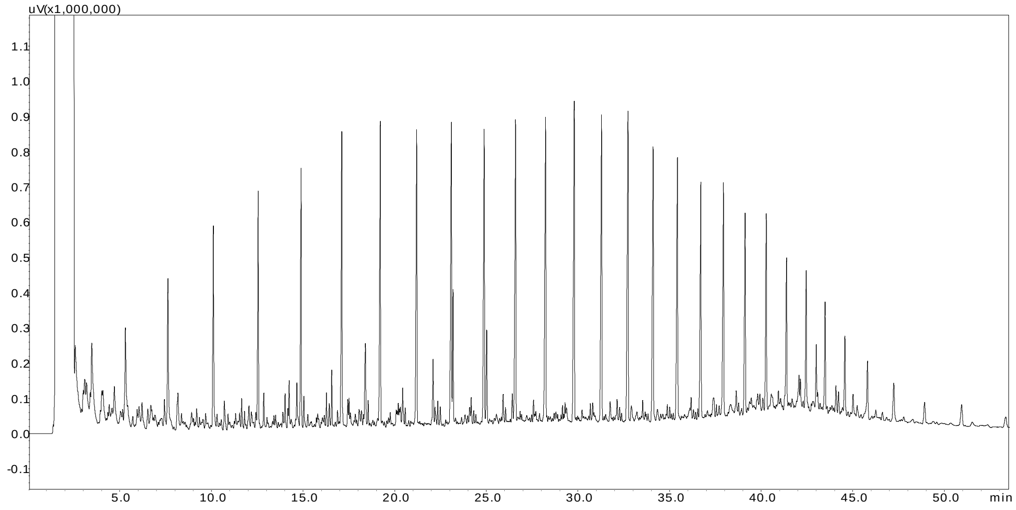

Fig.6. Suspected source, RR2010-4.

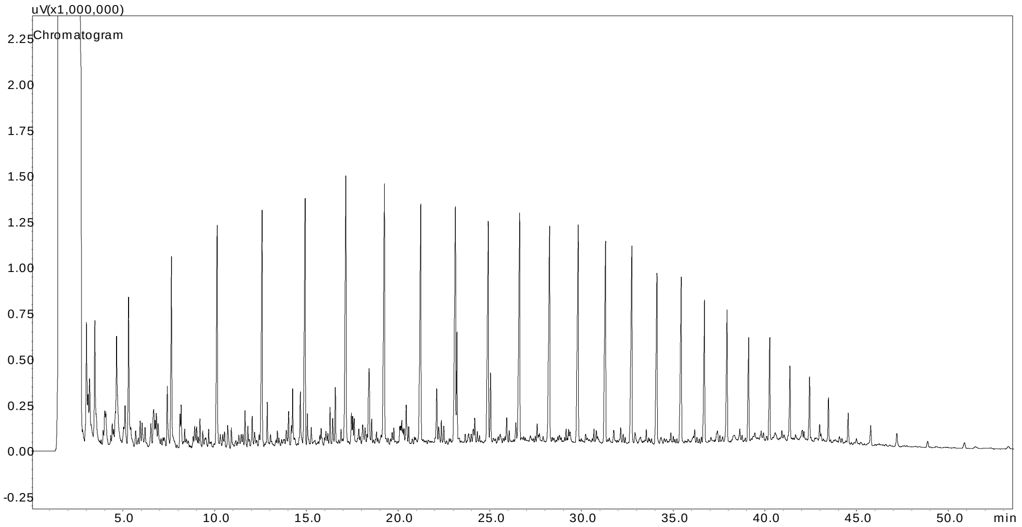

Fig. 7. Suspected source, RR2010-5.

In this Round Robin test, most participants went through the GC-FID screening, while some participants went directly to GC-MS. From the GC/FID chromatograms (see Table 4) most participants identified the difference of RR2010-1 with the other samples by the higher levels of alkylated naphthalenes and aromatics. Some participants concluded that RR2010-1 was probably a fuel oil, while RR-2010-2 and RR-2010-3 were probably weathered crude oils in this round.

From the GC/FID chromatogram peak profile, many participants identified the evaporation or biodegradation of RR2010-2 and RR2010-3, based on the relative increase of the isoprenoids.

Some participants eliminated RR2010-1, but to determine the oil type, they still continued to the GC-MS analysis. Only one participate did not analyze sample 1 with GC-MS. Most participants did not eliminate any samples in this round, even is they already found the difference, but did not get the final conclusion and put all samples to GC-MS analysis, some participants also used GC-MS full scan to get more information.

The GC-FID screening results are summarized in Table 4.

Conclusion The results of the GC-FID analyses show significant differences of RR2010-1 with the other samples, it may be a HFO. No significant differences are found between samples RR2010-2, RR2010-3, RR2010-4 and RR2010-5 From the GC/FID chromatogram peak profile, it could been concluded that RR2010-2 and RR2010-3 were affected by evaporation or biodegradation.

For a further determination of the oil type, and comparison of the spill oil samples, all samples should go to the next step: the GC-MS analysis.

Table 4. GC-FID Screening Results.

Participants	Tentative classification oil type and reason	Determinated the degree of weathering?	Eliminated any samples?
Lab 1	Yes, abundant remains of aromatic compounds	Not mentioned	Yes, RR2010-1 was eliminated, but go through GC-MS for determine oil type
Lab 2	No	No	No
Lab 3	Yes, abundant remains of aromatic compounds	Yes,	No
Lab 4	Did not use GC-FID		
Lab 5	No	Yes	No, although difference was found
Lab 6	Yes, The presence of high levels of naphthalene and 1-naphthalenes	Yes, RR2010-3was more weathered than RR2010-2, RR2010-3 was affected by biodegradation	No, all samples were directly analysed with FID and MS for determine oil type
Lab 7	Yes, spill sample 1 contains quite a lot of aromatics and may contain as well some heavy fuel oil.	Yes	No, although difference was found
Lab 8	No	Yes	No, although difference was found
Lab 9	Did not use GC-FID		
Lab 10	Yes, The GC-FID profiles, carbon ranges of GC-TPH, n-alkane distribution, and the characteristic shapes of the UCM hump	Yes	No, although difference was found
Lab 11	Yes, sample 1 is a HFO without any doubt, for high concentrations of aromatics	Yes	No
Lab 12	No, could not determine HFO or special crude oil	Yes,	No
Lab 13	Did not use GC-FID		
Lab 14	No	No	No
Lab 15	No, could not determine HFO or weathering crude oil	Yes，RR2010-3 was more weathered than RR2010-2, RR2010-3 was affected by biodegradation	No, although difference was found
Lab 16	Did not use GC-FID		
Lab 17	No	Yes	No, although difference was found
Lab 18	No	Yes	No, even if non-match was made
Lab 19	Yes,	Yes, A relative increase of the isoprenoids indicates biodegradation.	No, no final conclusion was made by GC-FID

Lab 21	Yes, The GC-FID profiles, carbon ranges of GC-TPH, n-alkane distribution, and the characteristic shapes of the UCM hump, RR2010-1 is likely a mixture of weathered crude oil with other type of oil.	Yes	No, although difference was found
Lab 22	Yes, In sample 1 can be seen distinct clusters of isomers from cracking processes	Yes	No, although difference was found
Lab 23	Yes, distillate range aromatic compounds	Yes, RR2010-3 was more weathered than RR2010-2, RR2010-3 was affected by biodegradation	No
Lab 24	Not mentioned	Not mentioned	Yes, RR2010-1 was eliminated, not go through GC-MS

5 GC-MS Evaluation

5.1 OIL TYPE

According to version 51 of CEN-TR 2v2 (this version has been send to CEN for acceptation), the GC-FID can be used to get a tentative classification to a type of the oil type, but a GC-MS analysis is necessary for confirmation. In version 51, HFO is described as follows:

Heavy fuel oil is a residual product of a refinery. It may have gone through a cat cracker and as a result the aromatic patterns can have been changed (sometimes becoming more or less standardized). As a result the methylphenantrene pattern has changed, the concentration of methylanthracene has increased significantly and the concentration of retene reduced strongly.

The results of the oil type determination are listed in Table 5.

Table 5. Oil Type identification.

Participant	RR2010-1	RR2010-2	RR2010-3	RR2010-4	RR2010-5
Lab 1	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 2	Cracked oil	Crude oil	Crude oil	Crude oil	HFO
Lab 3	HFO	Weathered crude oil	Weathered crude oil	Weathered crude oil	HFO
Lab 4	Mixture	Crude oil	Crude oil	-	-
Lab 5	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 6	Refinery product that has many aspects of an HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 7	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 8	HFO	Crude oil	Crude oil	Crude oil	-
Lab 9	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 10	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 11	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 12	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 13	-	-	-	-	-
Lab 14	HFO	Weathered crude oil	Weathered crude oil	Crude oil	Crude oil
Lab 15	Strong weathering Light Fuel / Heavy Fuel Oil	Light Fuel	Strong weathering Light Fuel	Light Fuel	Light Fuel
Lab 16	HFO	Crude oil	Crude oil	Crude oil	-
Lab 17	Shale oil	Crude oil	Crude oil	Crude oil	Crude oil
Lab 18	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 19	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 21	A mixture of weathered crude oil and weathered light refined petroleum product (probably gasoline range fuel).	Crude oil	Crude oil	Crude oil	Crude oil
Lab 22	HFO	Crude oil	Crude oil	Crude oil	Crude oil
Lab 23	HFO	Weathered crude oils	Weathered crude oils	Crude oil	Crude oil
Lab 24	-	-	-	-	-

RR2010-1 was classified as HFO by all participants, RR2010-5 was classified as HFO by some participants, RR2010-2, RR2010-3, and RR2010-4 were classified as crude oil by nearly all participants.

5.1.1 RR2010-1

The GC-MS chromatograms of RR2010-1 are shown in Fig. 8.

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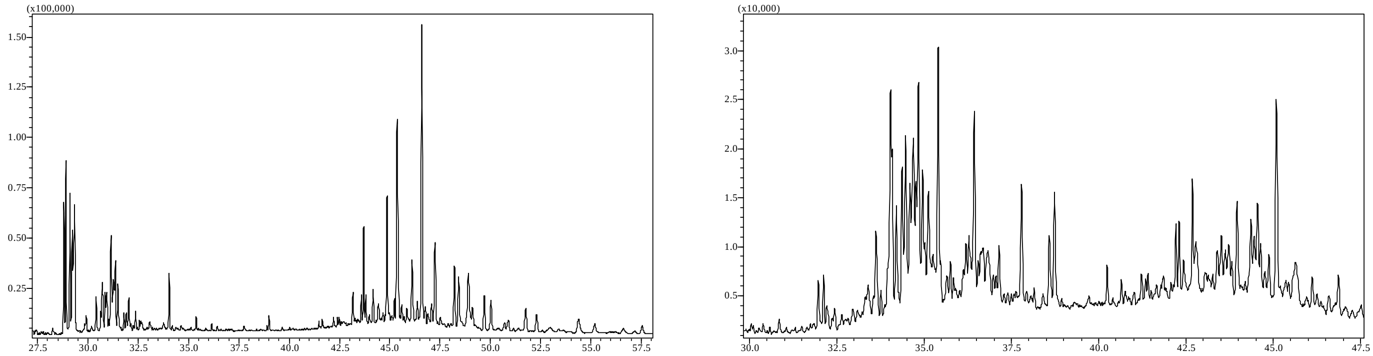
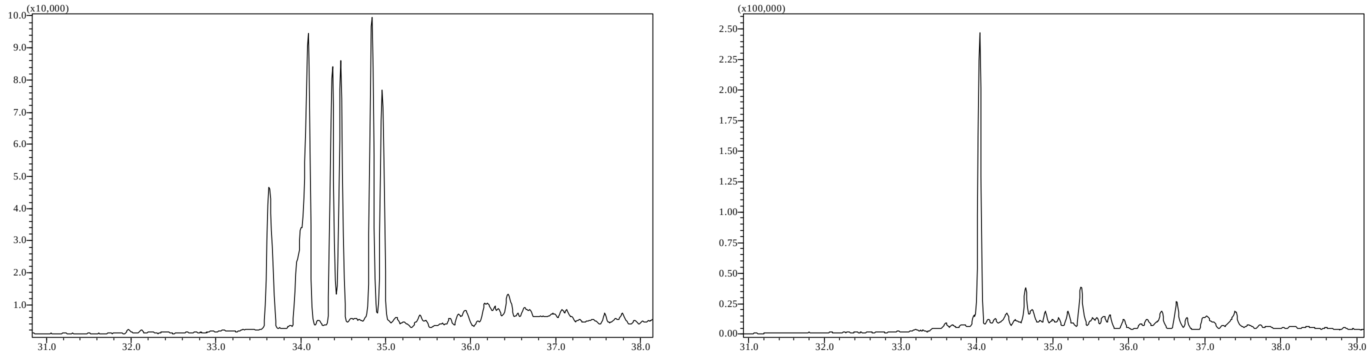


M/Z 191 **M/Z 217**



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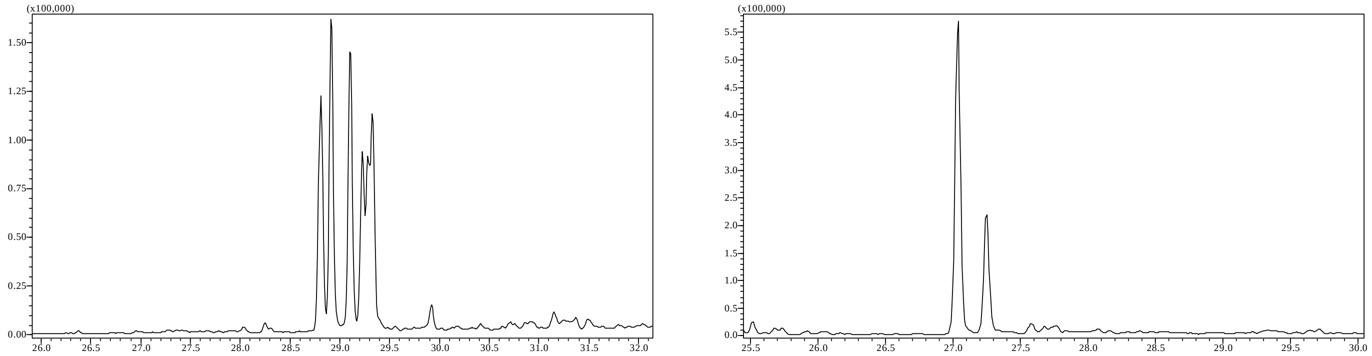
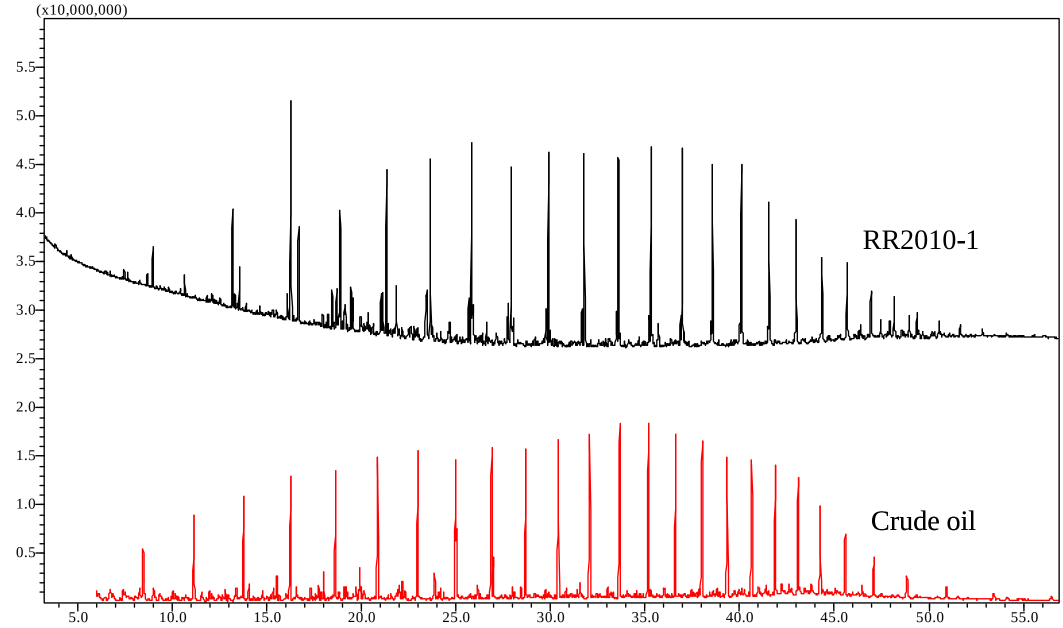


M/Z 192 **M/Z 178**

Fig. 8. GC/MS chromatograms of RR2010-1.

In order to get more information about RR2010-1, a full scan analysis was conducted, and compared with an ordinary crude oil (Shown as Fig. 9).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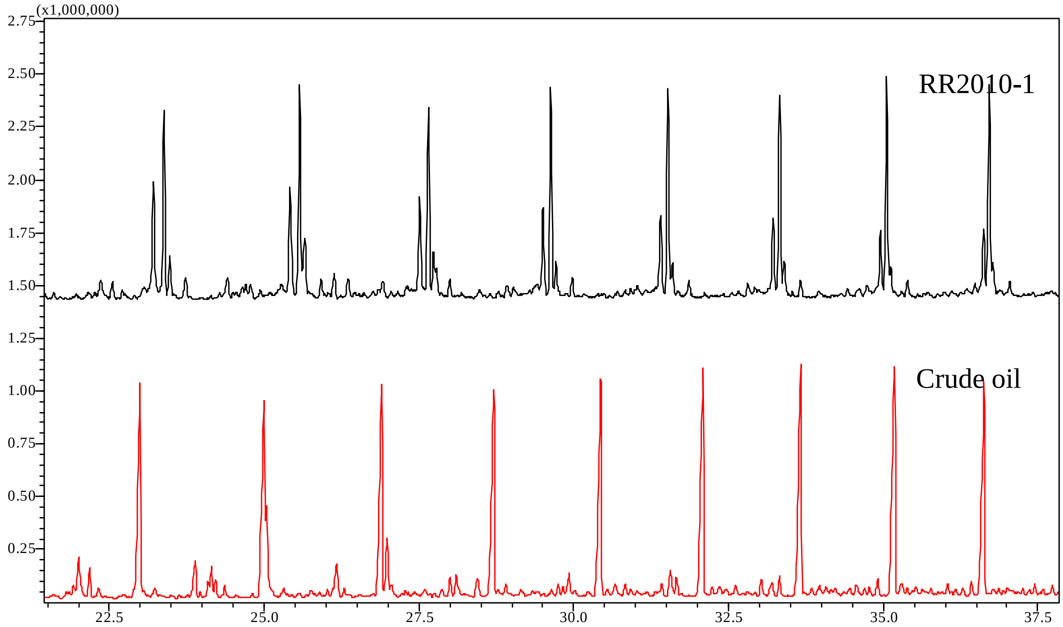
RR2010-1
Crude oil

TIC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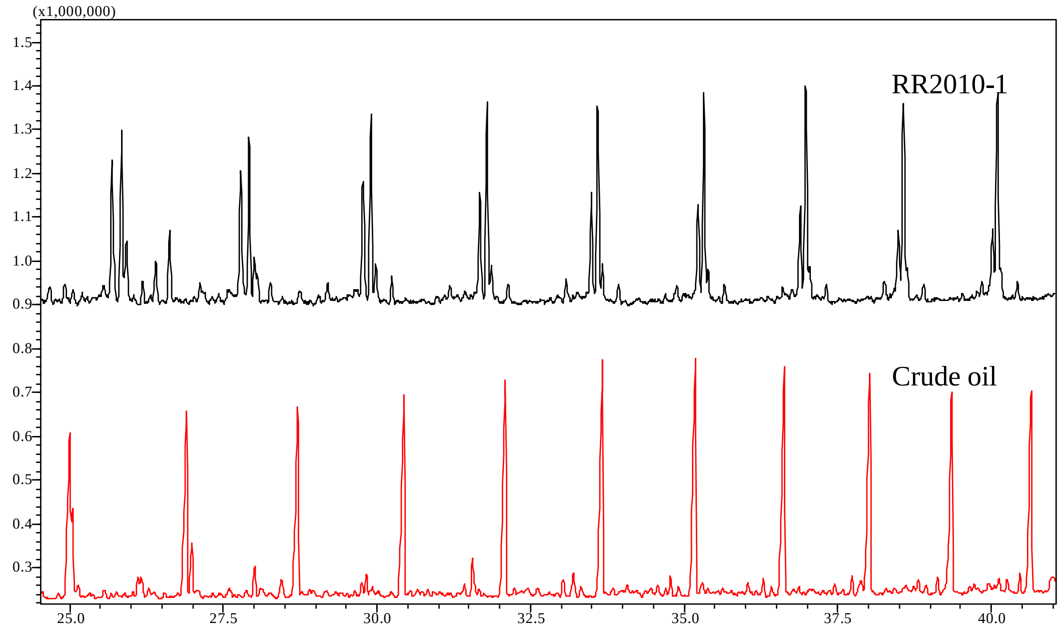
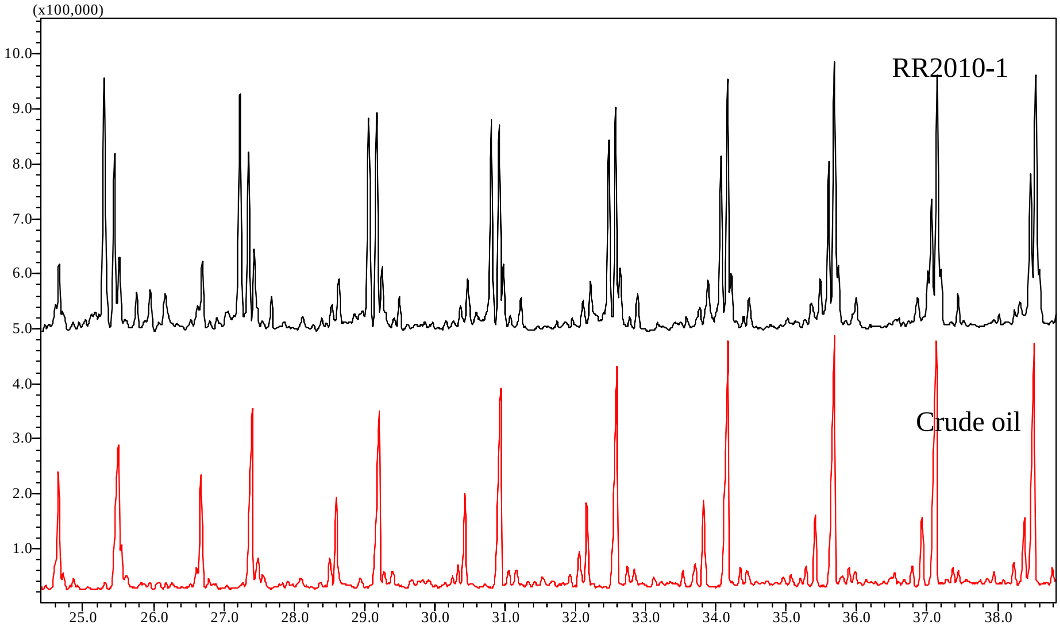
25.0
27.5
30.0
32.5
35.0
37.5
RR2010-1
Crude oil

M/Z 55



M/Z 69



M/Z 83

Fig. 9. GC/MS chromatograms of RR2010-1 and crude oil.

It was mentioned in chapter 3, that RR2010-1 is a real spill sample, and we had difficulties to sort this oil into the right product-category. Such kinds of spills were found more often in our sea-areas. Of course it is a HFO –at first sight. But results were contradictory: high aromatics were found already in the gas-chromatogram of this sample, which, for sure, originate from cracking, but this oil also contains a very high amount of retene, which –according to the description of the oil types as given in the CEN/TR- should not have been present.

Generally, and according to the high aromatics in the gas-chromatograms, sample 1 could have immediately been ruled out as non-matching to the other samples (first step in the Analytical Scheme of the CEN/Tr). Some participants did it. But most participants analyzed this sample further, and found the high retene peak. Additionally, some participants also found high concentrations of unsaturated alkenes over the whole boiling range, which eluted just before the n-alkanes with corresponding carbon numbers. This could have been seen in the gas-chromatograms already, and could have been evidenced by the m/z 83 profile. This is uncommon in HFOs, which contain residues from cracking. Although bonds are broken by the cracking process, and aromatics and actually olefines are produced, normally only the aromatics remain, because the olefines normally react very rapidly, and thus may only be regarded as intermediate products.

So, this spill was separately discussed in this chapter, with focus on the identification of oil type. The results of some of the participants concerning the oil type of RR2010-1 are summarized below:

- Based on the GC-FID results, the sample from the Harbor was not analyzed by the GC-MS method described in the CEN Guideline. In this case, a full scan analysis was performed just to confirm the identity of the aromatic clusters. Among other PAHs (i.e., manly naphthalenes, phenanthrenes), an unusual high peak of retene was observed. The presence of this compound is not common in HFOs. The possible explanation is a background presence as some areas in the Bohai Sea present high level of this compound (Bixiong et al., 2006). This issue was not further investigated since this sample was clearly different of the others and the location of the harbor is unknown **(Lab 1)**.
- The screening results show that RR2010-1 is a mixture, it contains a crude oil, unsatured aliphatics (not only 1-alkenes but also 2-alkenes and others) and the naphtalenes (C0-C4) have unusual high concentrations compared to the aliphatics. **(Lab 4)**
- The samples were also analyzed by HTGC (high temperature gas chromatography) / FID (see appendix 2 for conditions and appendix 4 for chromatogram), and the nature of the sample RR2010-2 to RR2010-5 seemed to be confirmed (lack of residue of distillation, in agreement with crude oils). RR2010-1 seems to be composed of a heavy fraction, which appears not clearly (not a vacuum residue), and then could have been obtained following a visbreaking process. **(Lab 5)**
- RR2010-1 is an unknown type of oil. It is probably a type of HFO from a refinery with an uncommon type of cracking process. **(Lab 6)**
- According to the visual inspection of the GCs (Analytical Scheme, step 1.1), sample 1 is ruled out immediately as non matching to all other samples because of the presence of high concentrations of aromatics in the lower and mid-boiling region (M-naphthalenes, DM-naphthalenes etc.), which originate from cracking processes. As also compounds up to the highest boiling range are present, sample 1

is a HFO without any doubt. A closer look at the GC of sample 1 reveals that peaks are found just in front of every n-alkane. By means of a full-scan run, these peaks were identified as alkenes (olefines). Also a high retene-peak is found. A special refinery process, not conducted in European refineries, may be an explanation for these peculiarities, and mixing of cracking products with products from other refinery streams. **(Lab 11)**

- The GC profile of spill sample RR2010-1 showed a bimodal envelope of alkane peaks with prominent naphthalene and many alkyl naphthalene compounds, and an unusually large 2-methyl anthracene peak for C1 phenanthrenes(m/z192), As well, the first pair of peaks for M-phenanthrenes cluster were more abundant than second pair of peaks. Several alkenes from about C13 to C22 were also detected in this sample. Alkenes are not normally found in crude oils but are formed when crude oil is cracked in the refinery. This suggests sample RR2010-1 contains a heavy fuel oil, however, there was contradictory date regarding the identification of the type of oil, namely the presence of the large retene peak which is usually reduced in heavy fuel oil (CEN/TR 15522-2 annex H4.22). The presence of retene may have been due to some unknown contamination. **(Lab 15)**
- Possibly the oil spill 1 is a shale oil. **(Lab 18)**
- RR2010-1 might be a heavy fuel oil (HFO), due to that the ion of chromatogram of C1-phenanthrenes (m/z192), contains a high content of methyl-anthracene, and that the first doublet is higher than second. A very distinct retene peak was observed in the ion chromatogram of C4-phenanthrenes (m/z234), which is uncommon in HFO(according to CEN2v2). However, it has earlier been seen that HFOs can content retene, possibly because of an incomplete cracking process. **(Lab 19)**
- Its GC-MS fingerprints reveal that this oil was probably mixed with refined petroleum products. For 2010-1 naphthalene and methyl-naphthalenes peaks are quite high but its light components are low, which indicates weathering and contribution of other type of oils such as gasoline or diesel. **(Lab 20)**
- RR2010-1 could contain a mixture of weathered crude oil and weathered light refined petroleum product (probably gasoline range fuel). naphthalene and methyl-naphthalenes in RR2010-1 is particularly high while its light components are in low abundance. This is unlikely a result of enrichment by weathering (i.e., evaporation or biodegradation), but rather probably a contribution from other type of oils (probably gasoline range fuel). Its GC-MS fingerprints further disclose this oil was probably contained refined petroleum products.**(Lab21)**
- In sample 1， heavy fuel oil (HFO) was found. In sample 1 can be seen distinct clusters of isomers from cracking processes (characterization by GC-FID). The cluster of isomeric M-phenanthrenes, for example, is typical of the high-temperature production of aromatics, Retene is not always present in HFO, but here we can see it in sample 1**(Lab22)**

- RR2010-1 is comprised of a heavy fuel oil. This is best evidenced by an excess of distillate range aromatic compounds (naphthalenes) indicating the presence of a cracked intermediate blending stock. Apparent “excess” C14-C15 n-alkanes evident in n-alkane profile (above) is due to co-eluting aromatics, and not excess n-alkanes (which is confirmed by a lack of excess n-alkanes revealed by the GC/MS m/z 85 pattern). **(Lab 23)**

At the annual meeting of the BonnOSInet group in Barcelona April 2011:

- Joan Albaiges (CSIC, Spain) remarks that without taking into account the retene peak, the distribution for Sample 1 and the presence of a range of alkenes is typically obtained after thermal treatment (alkenes are often seen in fire residues for example).
- Pierre Giusti (Total, France) comments that normally HFO is a mixture from different streams of a refinery, e.g. remains of the cat cracker is mixed with a light product (LCO) from the vacuum distillation, resulting in an HFO with the wanted viscosity and specifications. This could explain the retene content as the HFO will not only be coming from cracking.
- Pierre also informed that the best way to analyze, whether an oil sample is a crude oil or a mixture of oil products, is to use a high temperature simulated distillation with a metal column. See ASTM protocols D7169-05 and ASTM D2887. Compounds up to C100 can be eluted. In case of a crude oil the chromatogram shows a constant pattern, while in case of a mixture the chromatogram is more or less divided in sections

5.1.2 High temperature GC-FID measurements.

According to the suggestion of Pierre Giusti at the meeting, Paul Kienhuis has analyzed some oil samples with a High Temperature (HT) GC-column with a system that normally is used to analyze samples quantitatively on mineral oil in water, according to ISO-9377:

Column: DBHT-SIMDIS, L=10m; Fd=0.15 µm; id 0.53mm; flow 6 ml/min.

Temp. Prog: 43°C - 2 min - 43°C - 10°C/min - 400°C 10 min

Splitless injection of 10 µl at 375°C; FID detector with a HT jet at 425°C.

The HFO and RR2010 samples have been cleaned over Florisil before analysis.

The alkane standard (Fig. 10A) shows that the resolution of the alkane peaks is reduced due to the ID of 0.53 mm of the column, but also that some space is left between C44 and the moment that the column bleeding starts, indicating the high temperature properties of the column phase.

A blank of dichloromethane has been analyzed as 3rd injection after two standards with

Brent crude oil. At the end of the sequence for the second time a blank DCM has been analyzed. The results are compared in Fig. 10B. It is obvious that bleeding has been reduced and that some ghost peaks are present in the last analyzed blank. The chromatogram of the blank DCM closest to each sample in the sequence is used as overlay for the chromatograms shown in Fig. 10 and 11.

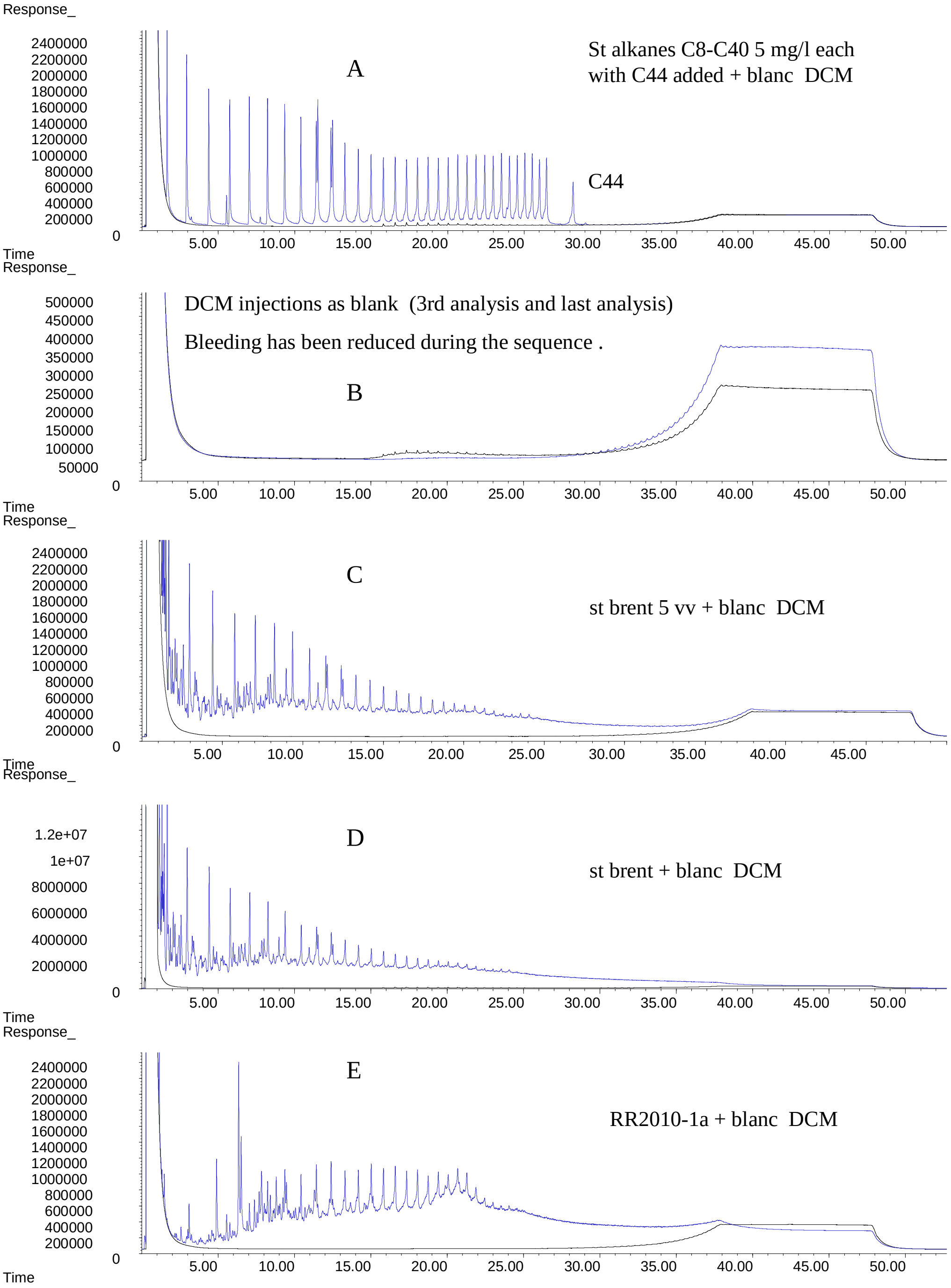


Fig 10. HT GC-FID analyses of a standard of alkanes, DCM injections as blank, Brent crude oil at two concentration levels and the first duplicate of RR2010-1. The chromatogram of DCM, analyzed closest to a sample is used as overlay to indicate baseline and bleeding.

The Brent crude oil has been analyzed at concentrations of 0.6 and 3 mg/ml to see whether this influences the pattern. Fig. 10C and D show that the concentration difference does not change the general pattern.

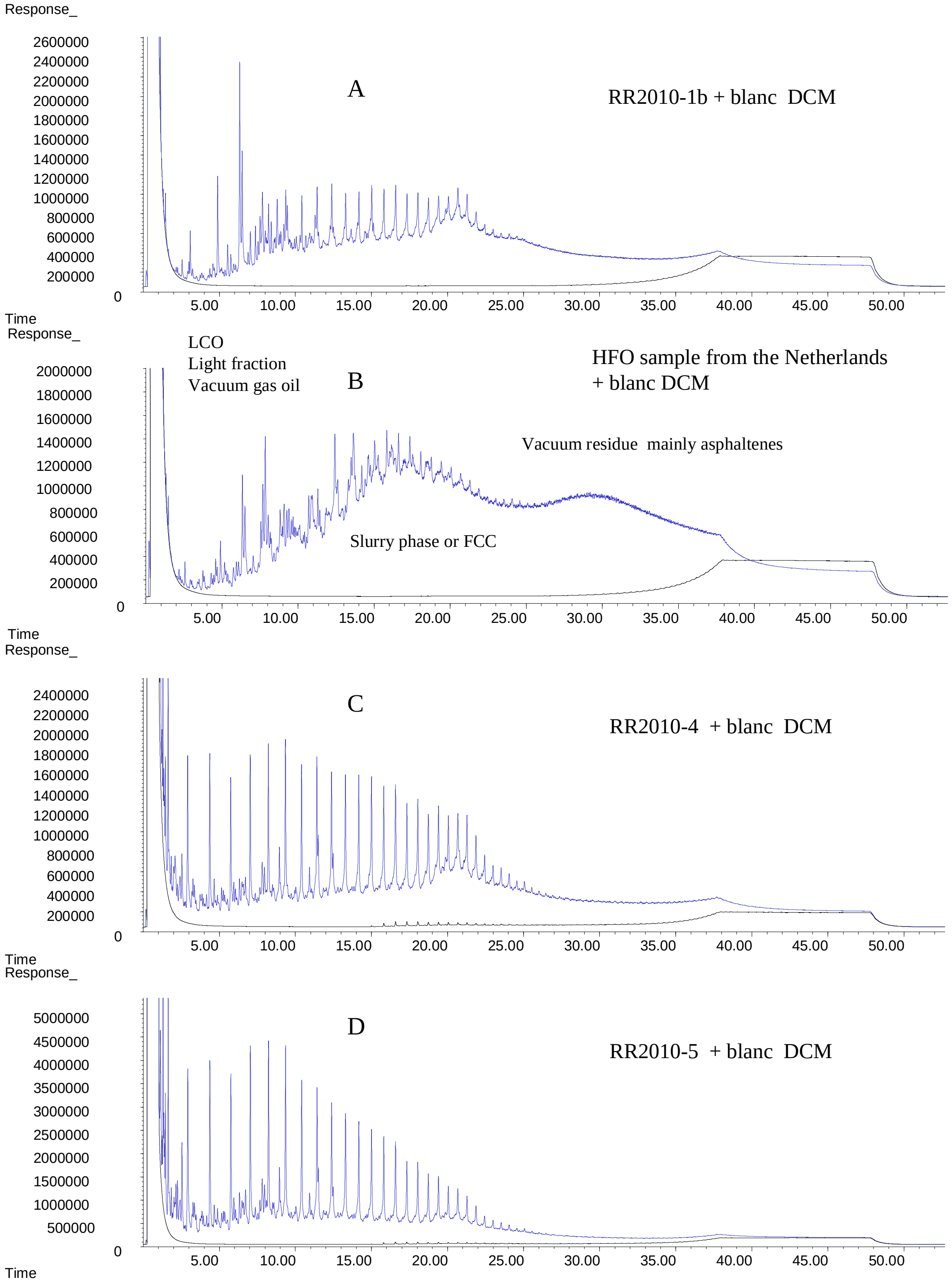


Fig. 11. HT GC-FID analyses samples RR2010-1 (second duplicate), a HFO sample from a case in the Netherlands and RR2010-4 and RR2010-5. The chromatogram of DCM, analyzed closest to a sample is used as overlay to indicate baseline and bleeding.

Sample RR2010-1 has been analyzed twice at the same injection concentration to see the variance between injections. Fig. 10E and 11A show very similar results.

In Fig. 11B the chromatogram of an HFO from a case in the Netherlands is shown. The sections mentioned by Pierre Giusti are very well visible.

Fig. 11C and 11D are from the two non-weathered crude oil samples of RR2010. Both show, besides a hump around a retention time of 21 min., a consequent pattern.

Comparing the two chromatograms of RR2010-1 with the crude oil samples (Brent, RR2010-4 and RR2010-5) and HFO sample shows that the lighter part is very similar to the HFO sample, but for the rest of the chromatogram of RR2010-1 the pattern doesn’t show the humps of the HFO sample.

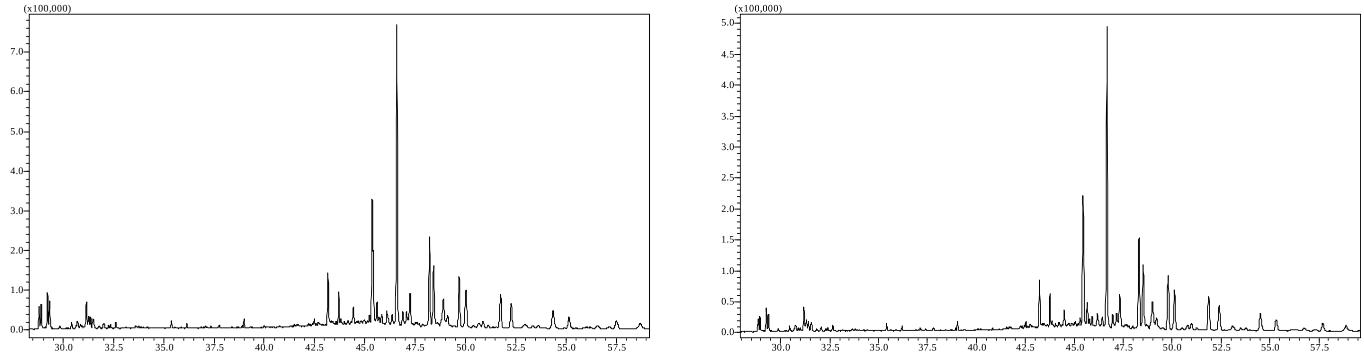
These results suggest that RR2010-1 could be a mixture of an atmospheric distillation residue of a straight run refinery that has been mixed with a light product to get the proper viscosity. See [2] for more information about the difference between a straight run refinery and a modern complex refinery.

This conclusion is however based on a limited knowledge of HT GC-FID analysis. E.g. the small decent at a retention time of 25 min for sample RR2010-1 could indicate that here a new part of a mixture starts.

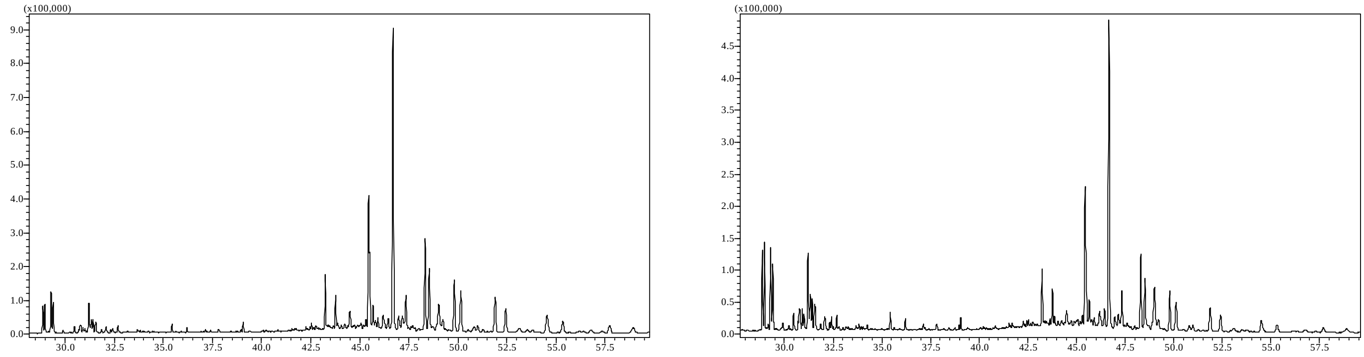
The results also show that a HT-GC-FID analysis can give additional information about the composition of an oil sample.

5.1.3 RR2010-2, RR2010-3, RR2010-4. RR2010-5

The GC-MS chromatograms of RR2010-2, RR2010-3, RR2010-4 and RR2010-5 are shown in Fig.12 to17.

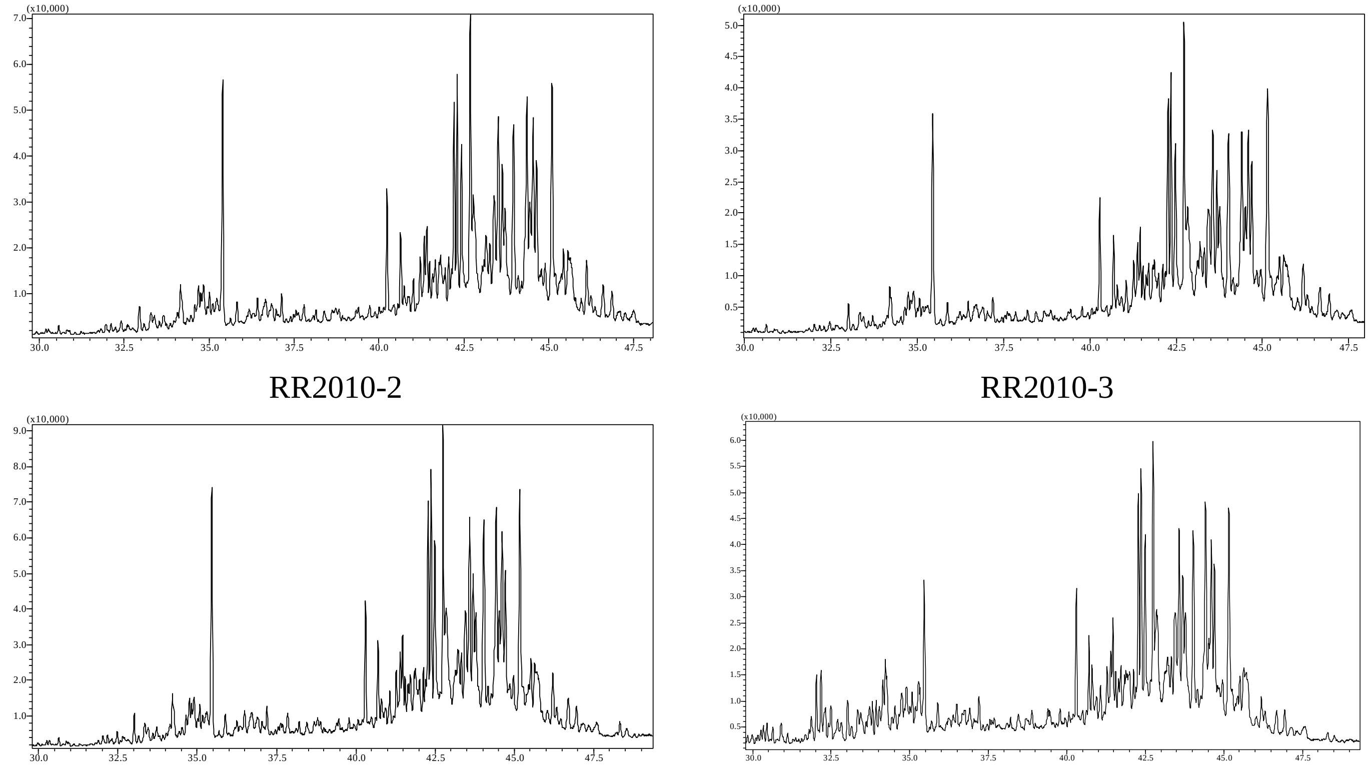


RR2010-2 RR2010-3



RR2010-4 RR2010-5

Fig. 12. Traces for m/z 191(hopanes) for the samples.



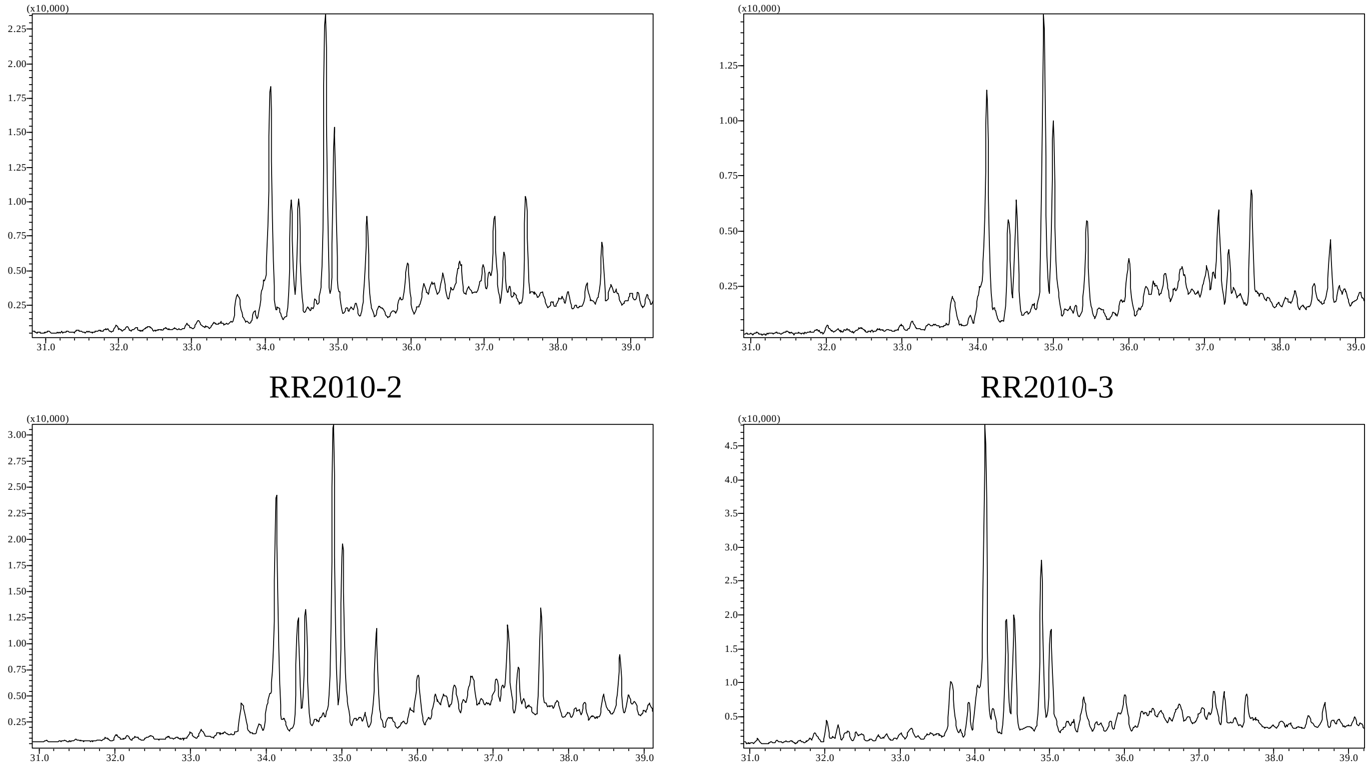
RR2010-2

RR2010-3

RR2010-4

RR2010-5

Fig. 13. Traces for m/z 217 (steranes) for all samples.



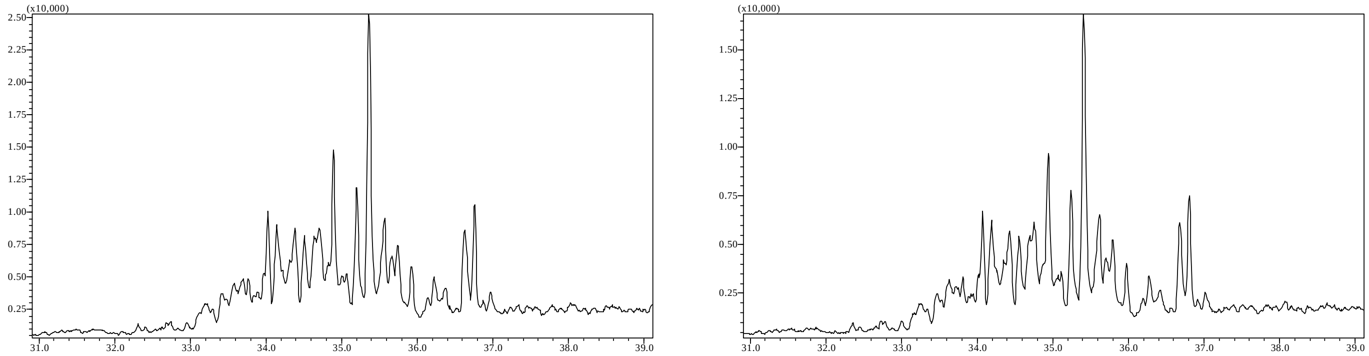
RR2010-2

RR2010-3

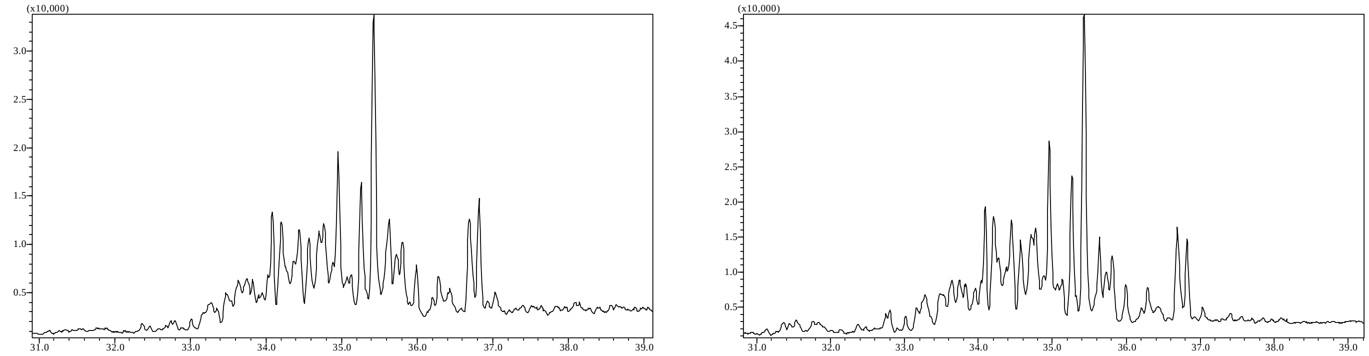
RR2010-4

RR2010-5

Fig. 14. Traces for m/z 216 (C1-fluoranthenes-pyrenes) for all samples.

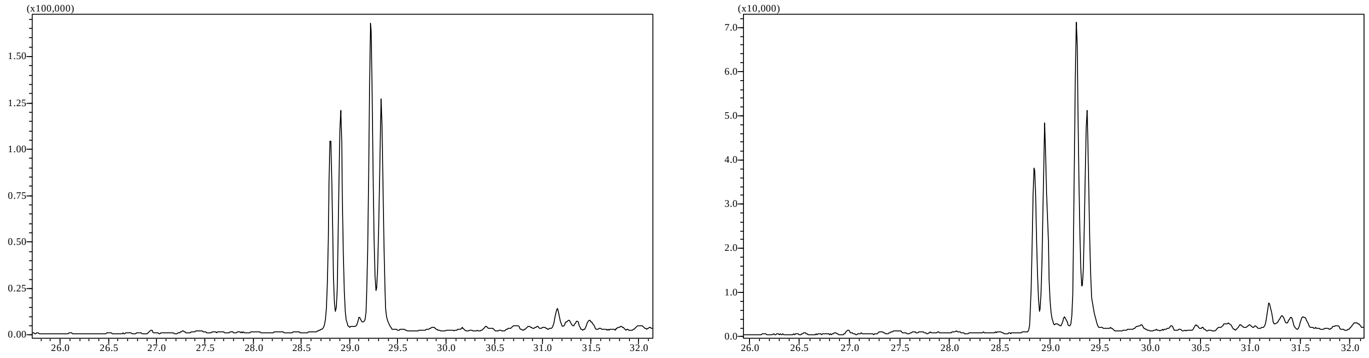


RR2010-2 RR2010-3

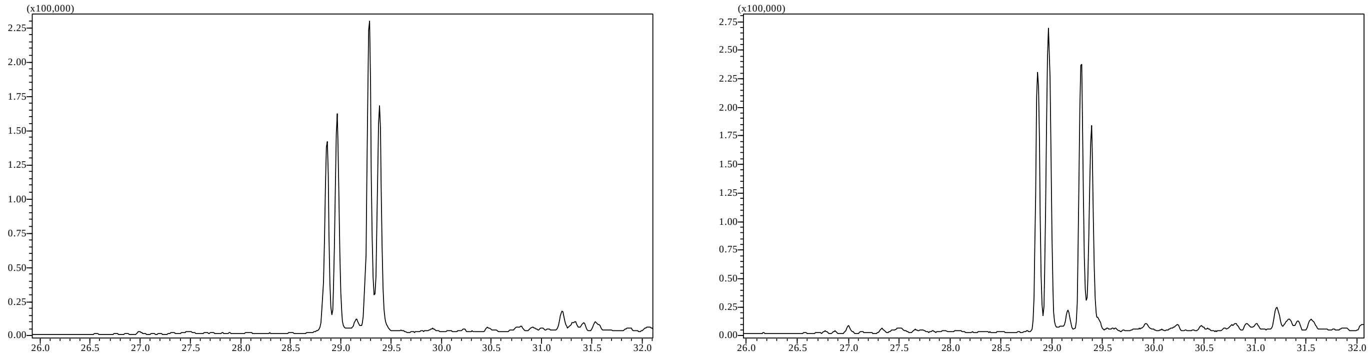


RR2010-4 RR2010-5

Fig. 15. Traces for m/z 234(C4-phenantrenes-anthracenes) for all samples.

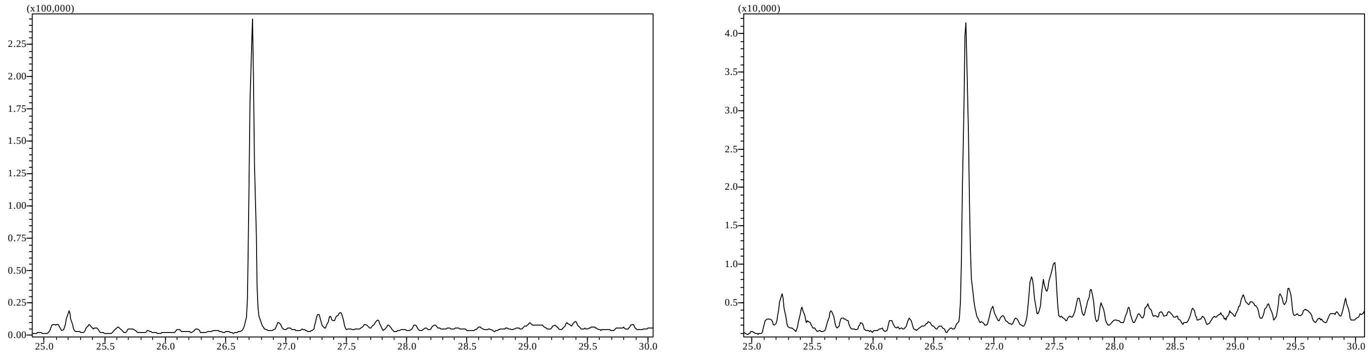


RR2010-2 RR2010-3

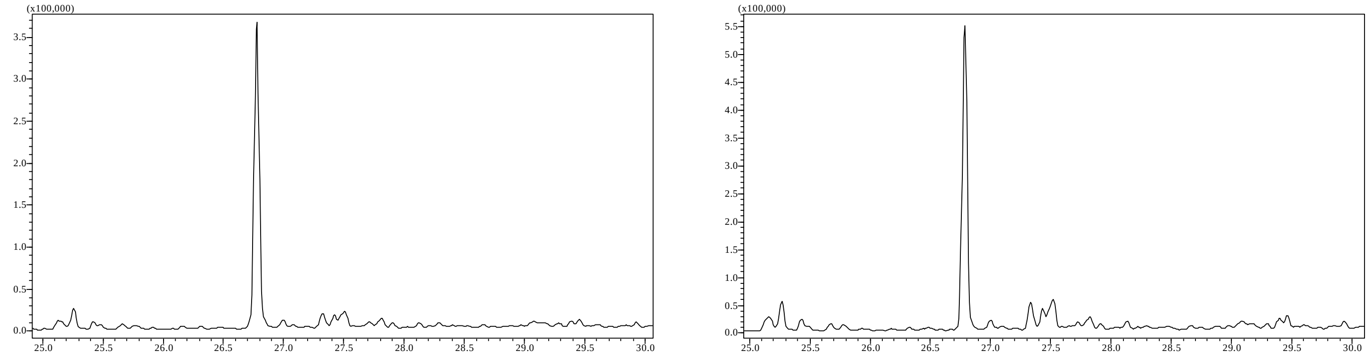


RR2010-4 RR2010-5

Fig. 16. Traces for m/z 192 (C1-phenantrenes-anthracenes) for all samples.



RR2010-2 RR2010-3



RR2010-4 RR2010-5

Fig. 17. Traces of m/z 178 (phenantrene and anthracene) for all samples.

All four samples are crude oils:

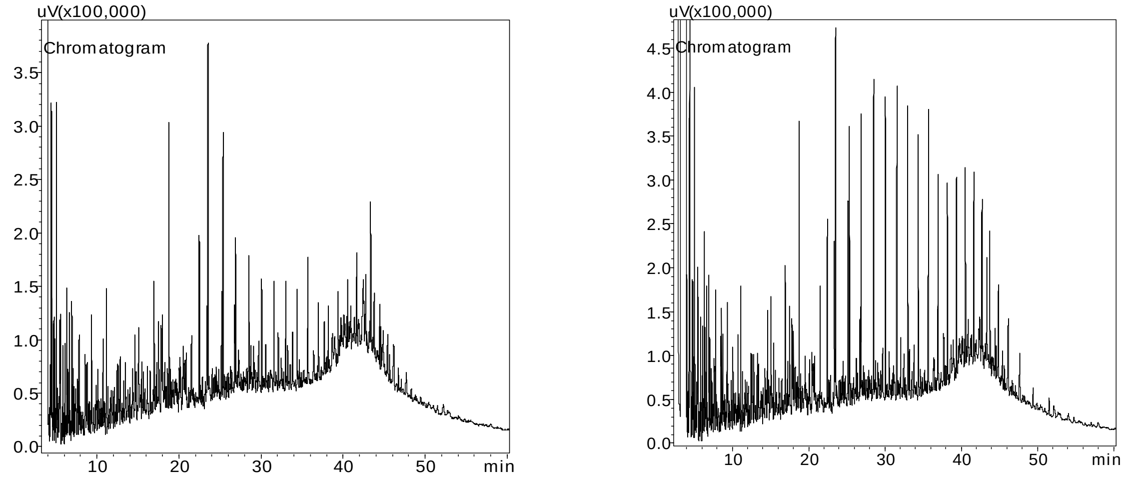
The ion chromatograms of m/z 192 contains only a small C1- anthracene peak, and the first doublet is lower than the second. The content of retene (m/z 234) is low. The suspected sources from the two pipelines are somewhat similar, but a few visual differences can be observed, especially in the PAH patterns (192 and 216). The oil from pipeline 1 shows more visual similarities to the shoreline spill, than the oil from pipeline 2.

Version 51 of CEN-TR 2v2 has the following description for HFO:

Heavy fuel oil is a residual product of a refinery. It may have gone through a cat cracker and as a result the aromatic patterns can have been changed (sometimes becoming more or less standardized). As a result the methylphenantrene pattern has changed, the concentration of methylanthracene has increased significantly and the concentration of retene reduced strongly.

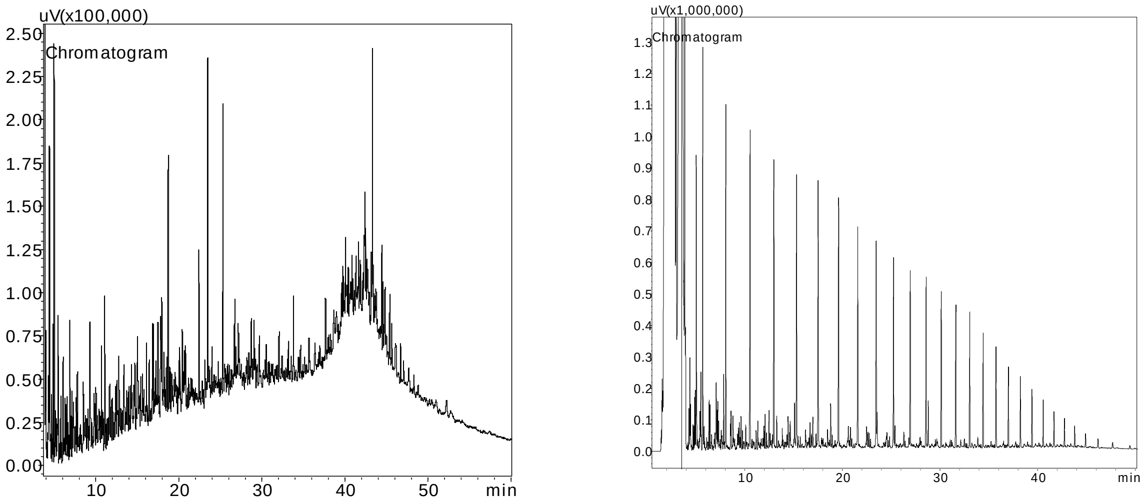
It can be concluded that the HFO definition is correct for the RR2010 samples 2 to 5, but not suitable for sample RR2010-1

We also found some crude oil samples that are quite similar to HFO. Some examples are given below: The GC-MS chromatograms of crude oils are show in Fig. 18 to 22.



B05 GC-FID

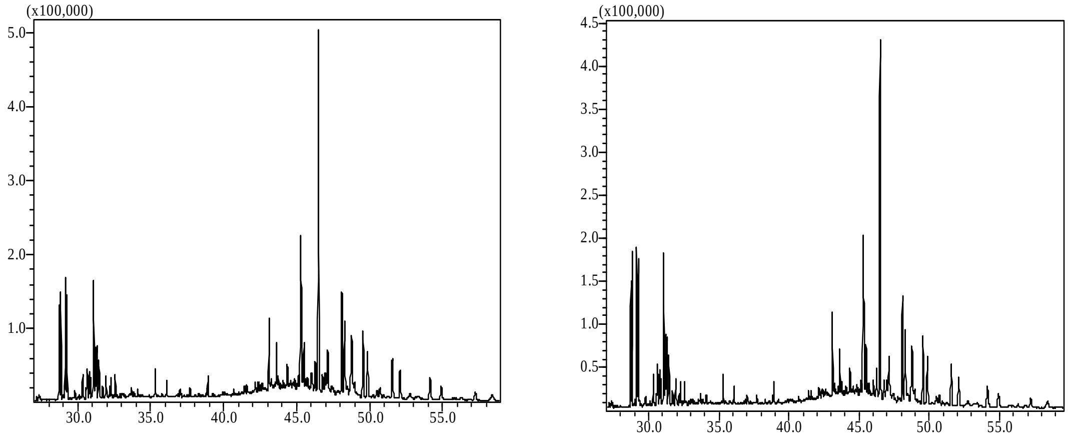
B06 GC-FID



B07 GC-FID

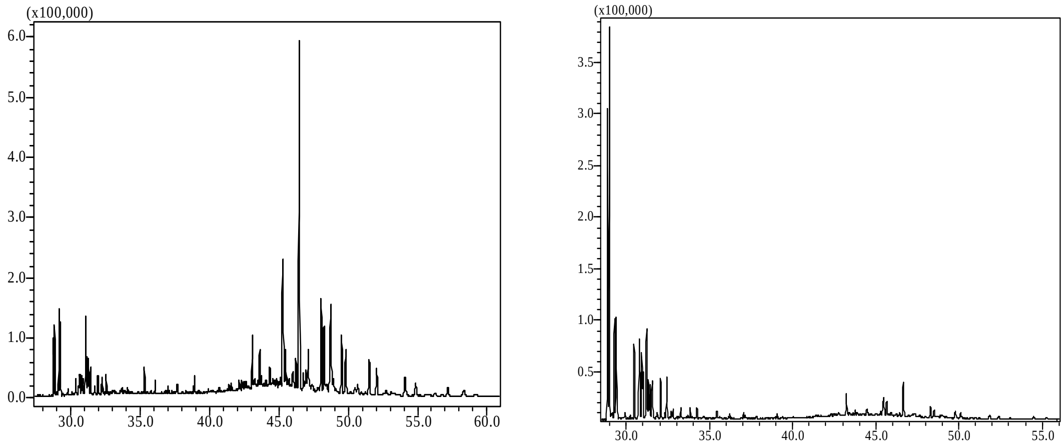
B08 GC-FID

Fig. 18. GC-FID chromatograms for four crude oils.



B05 m/z191

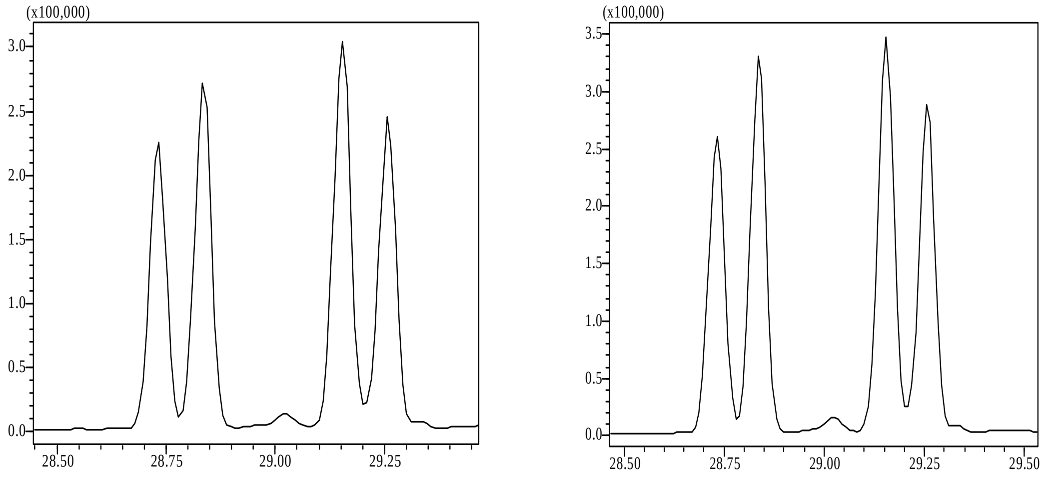
B06 m/z191



B07 m/z191

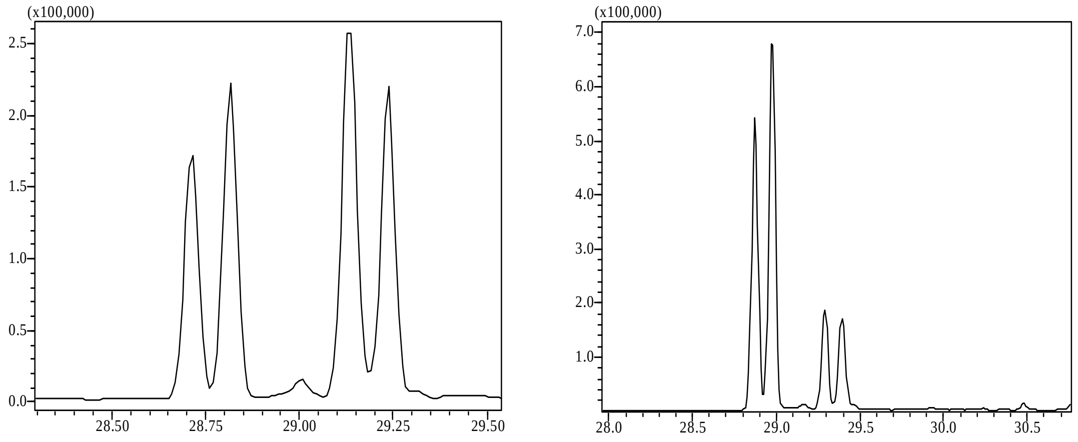
B08 m/z191

Fig. 19. Traces for m/z 191(hopanes) for four crude oils.



B05 m/z192

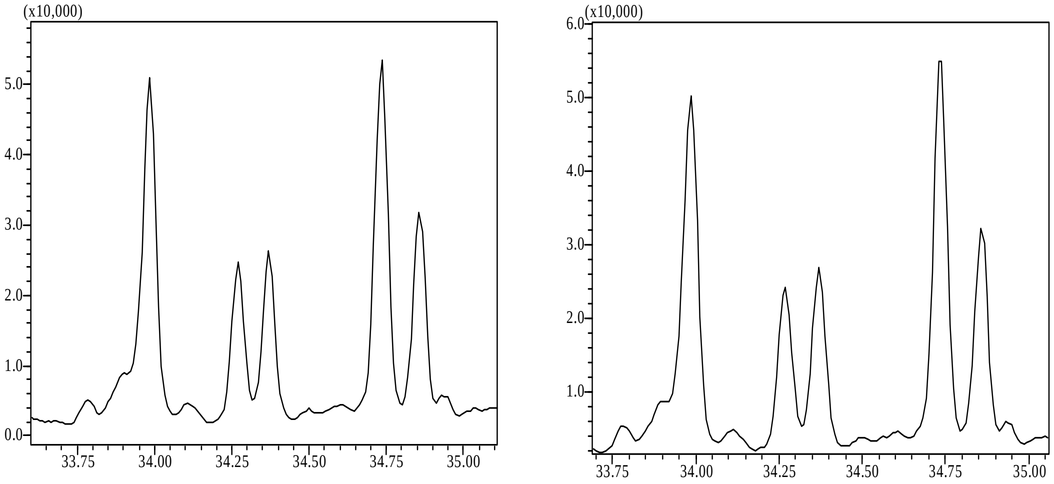
B06 m/z192



B07 m/z192

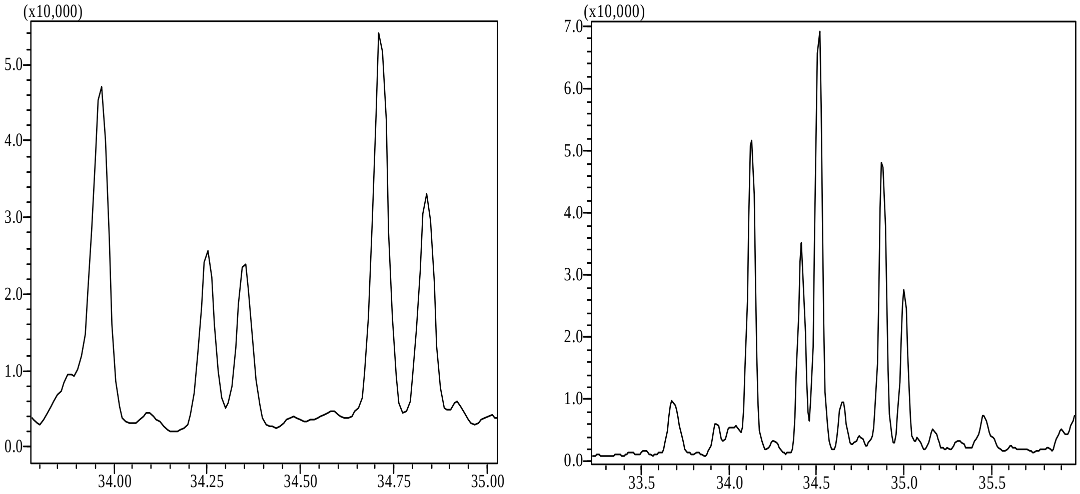
B08 m/z192

Fig. 20. Traces for m/z 192 (C1-phenantrenes-anthracenes) for four crude oils.



B05 m/z216

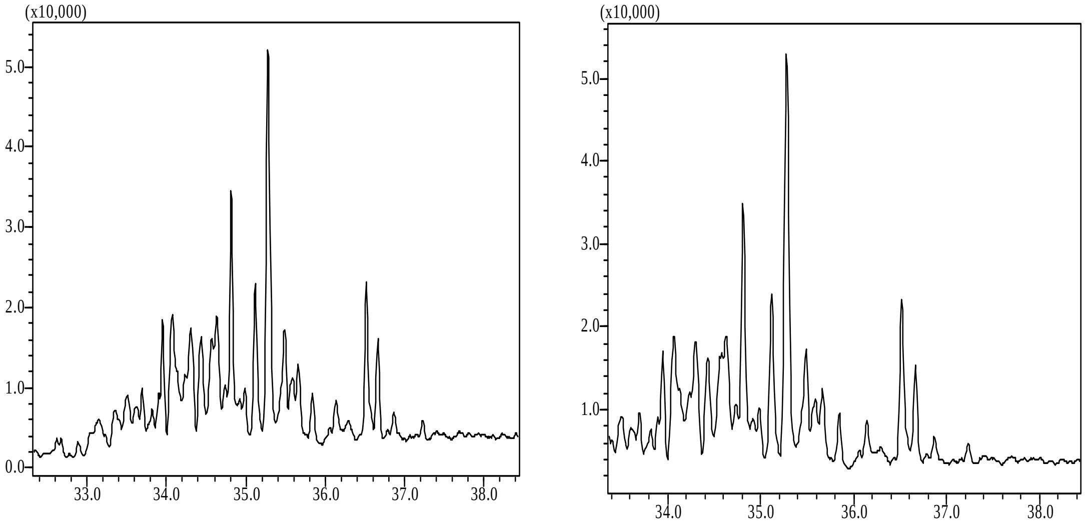
B06 m/z216



B07 m/z216

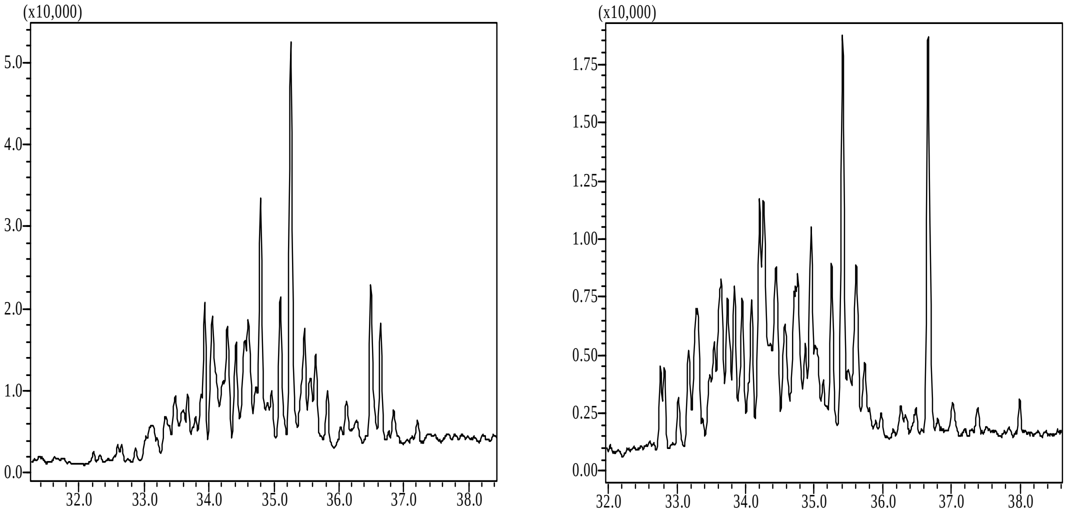
B08 m/z216

Fig. 21. Traces for m/z 216 (C1-fluoranthenes-pyrenes) for four crude oils.



B05m/z234

B06m/z234



B07m/z234

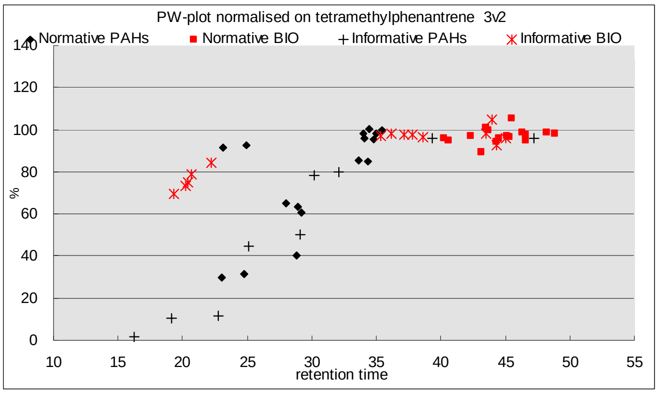
B08m/z234

Fig. 22. Traces for m/z 234(C4-phenantrenes-anthracenes) for four crude oils.

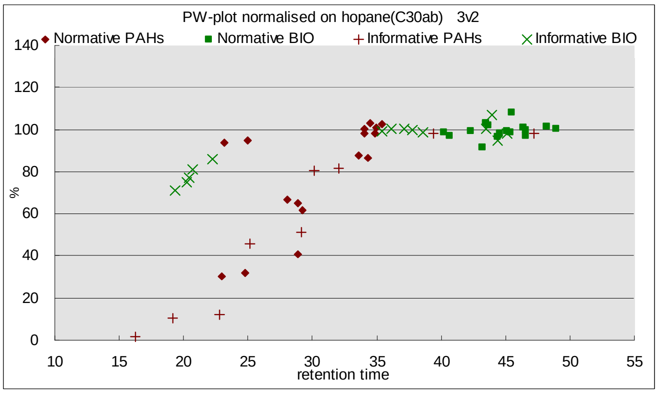
It can be concluded that: “methylanthracene has increased significantly” is the most important character of HFO, but there is not a quantity standard, and the methylphenantrene pattern may be affected by serious weathering. So it is necessary to work on a more detail identification standard for determining the oil type.

5.2 Comparison of the two beach sample (RR2010-3 vs RR2010-2).

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

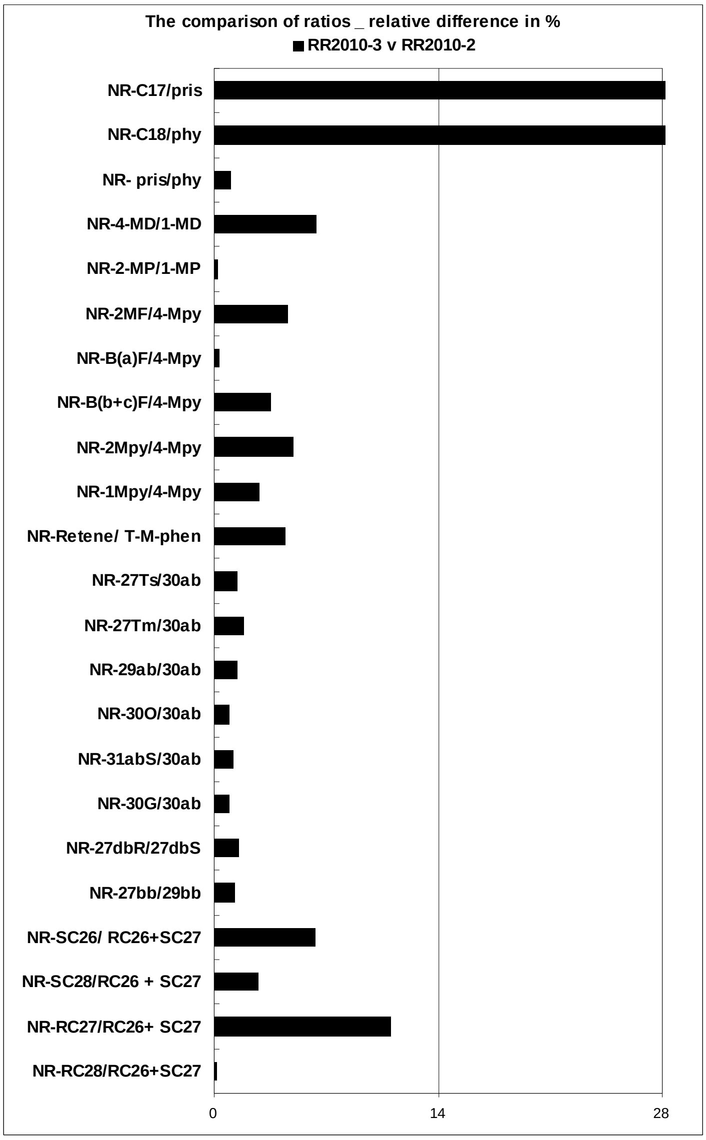


Fig. 23. Comparison of the RR2010-2 andRR2010-3: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The ratio graphs shows a good consistency between the two samples. Only the ratios C17/pristane and C18/phytane don’t match, which also was observed visually in the GC chromatograms. The MS-PW plot shows that the RR2010-3 is more weathered than the RR2010-2. The differences observed in the GC-PW plot are due to weathering and these two samples are from the same source.

For the sample comparison of RR2010-2 and RR2010-3, most participants reported that they have suffered with the different levels of evaporation (the lighter alkanes) and biodegradation (alkanes C17 and C18).

Lab 2 has done an extra experiment by washing sample 4 with water (Fig. 24) and has given an explanation of the behavior for the compounds in the PW-plot.

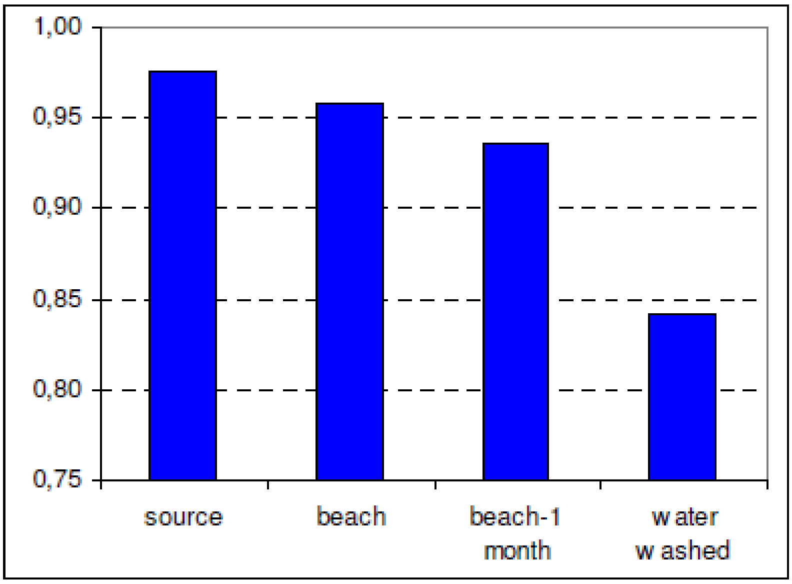


Fig. 24 Water washed effect on 2-Methyl / 1-methyl phenanthrene ratio (Lab 2).

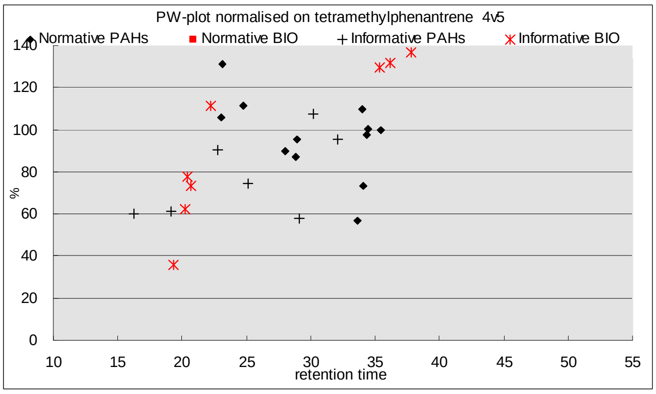
Lab 6 has also indicated and described the behavior of compound groups in the PW-plot in order to explain the PW-plot pattern: “a higher solubility in water (naphthalene and the C1- and C2-naphtalenes), but the variation is high.”.

Since the lab research was done in the underground chamber, little photo oxidation was occurred. Lab 6 reported it based on the C1-fluoranthenes-pyrenes analyzed by means of ion m/z 216 eluting after 35 min.

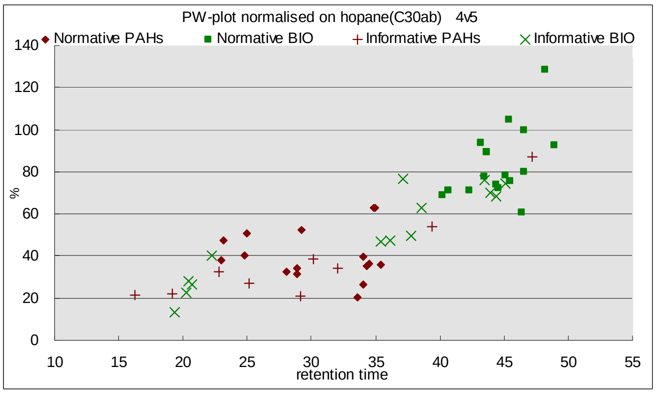
Conclusion: Positive Match

5.3 Comparison of the two suspected sources (RR2010-4 vs RR2010-5).

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

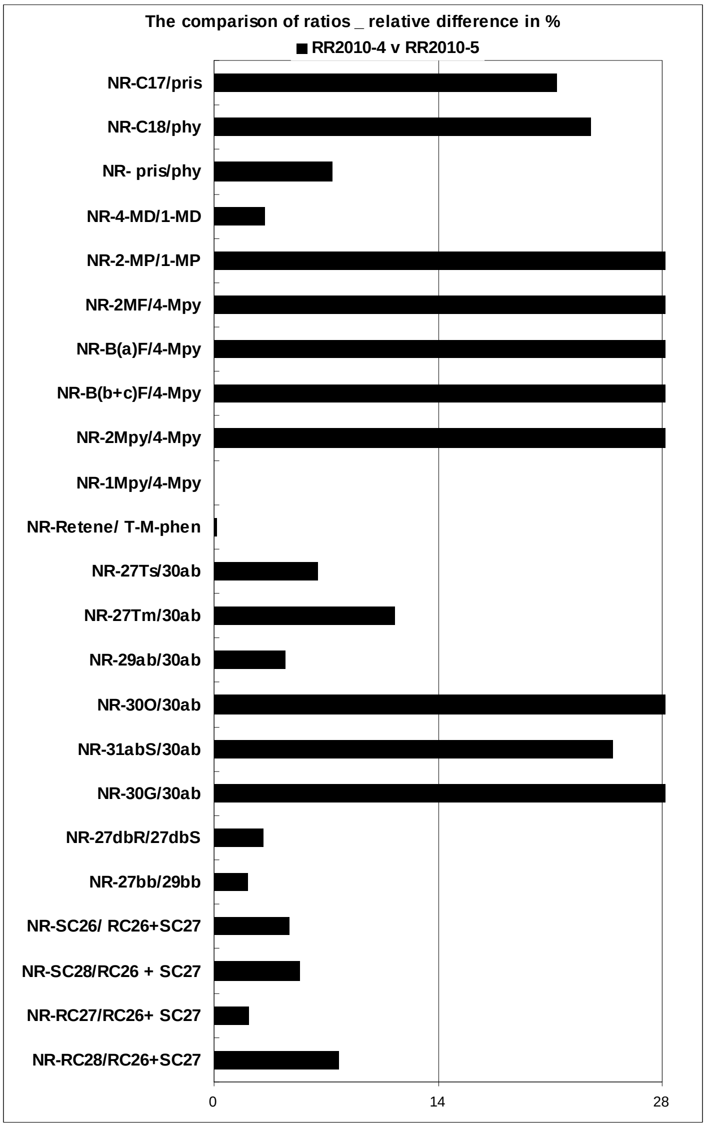


Fig. 25 Comparison of the RR2010-4 andRR2010-5: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

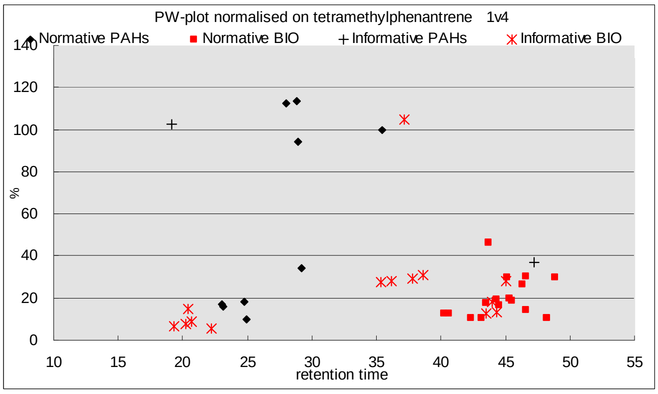
Discussion: The results confirm that the fingerprinting of the oils from the suspected sources is different.

Conclusion: Non-Match

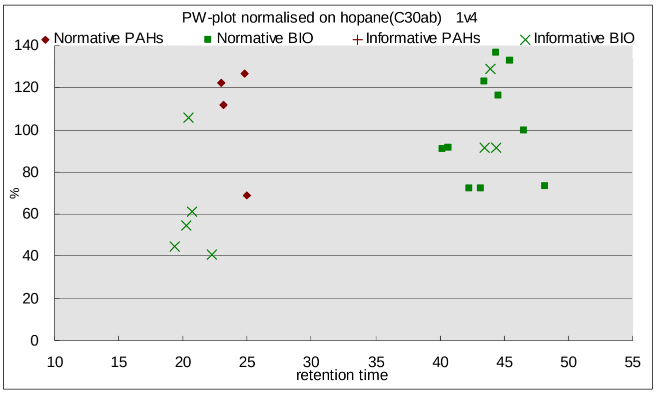
5.4 Comparison of spill samples and suspected sources

5.4.1 RR2010-1 vs RR2010-4

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

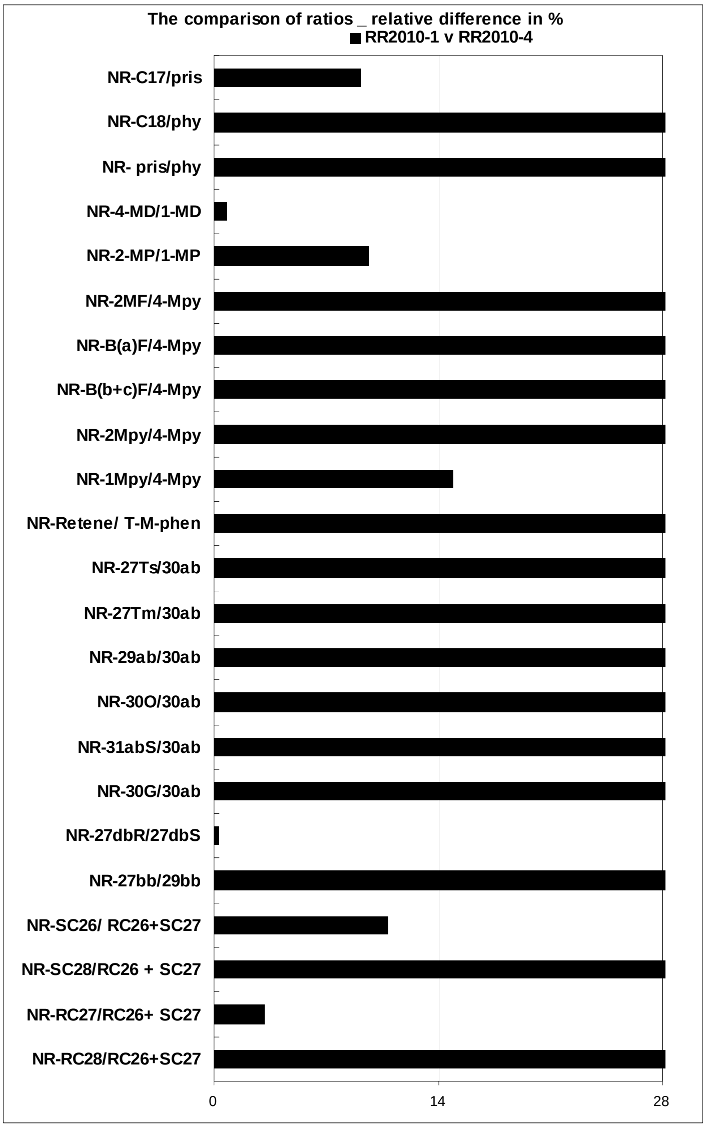


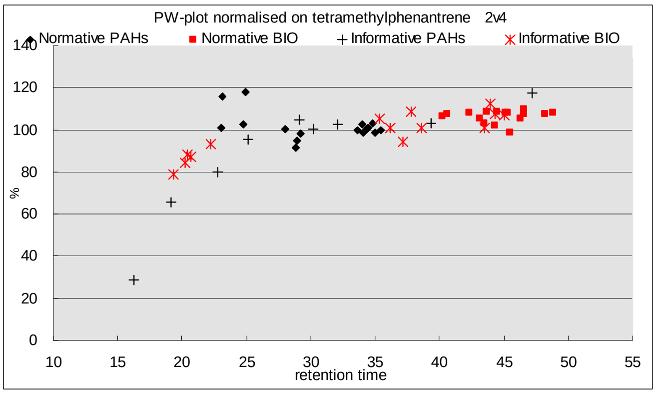
Fig. 26 Comparison of the RR2010-1 andRR2010-4: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: the results confirm that these two samples are from different sources.

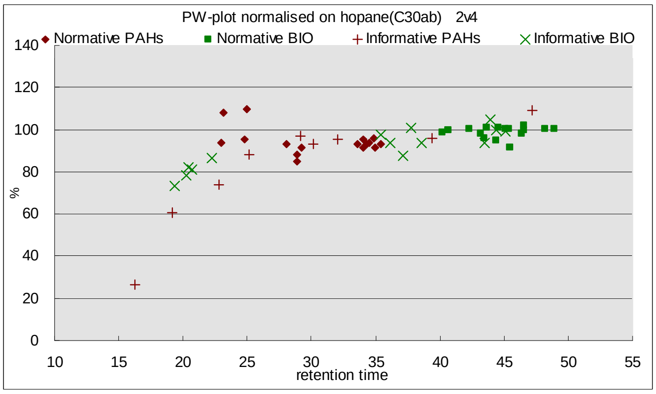
Conclusion: Non-Match

5.4.2 RR2010-2 vs RR2010-4

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

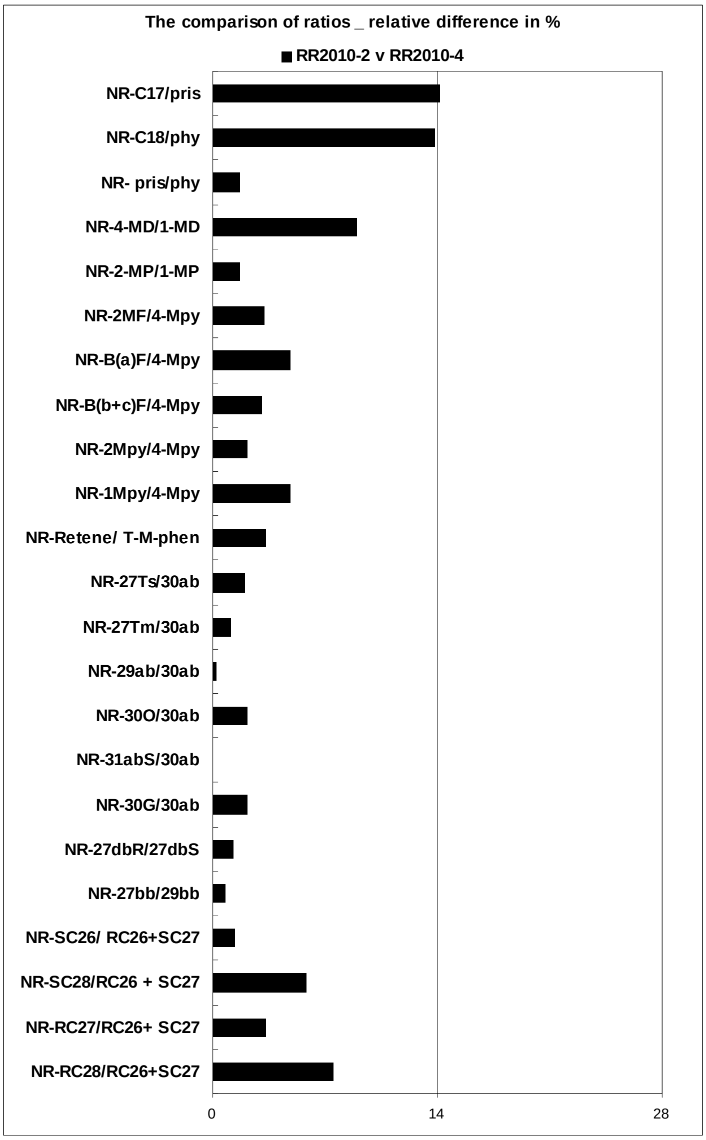


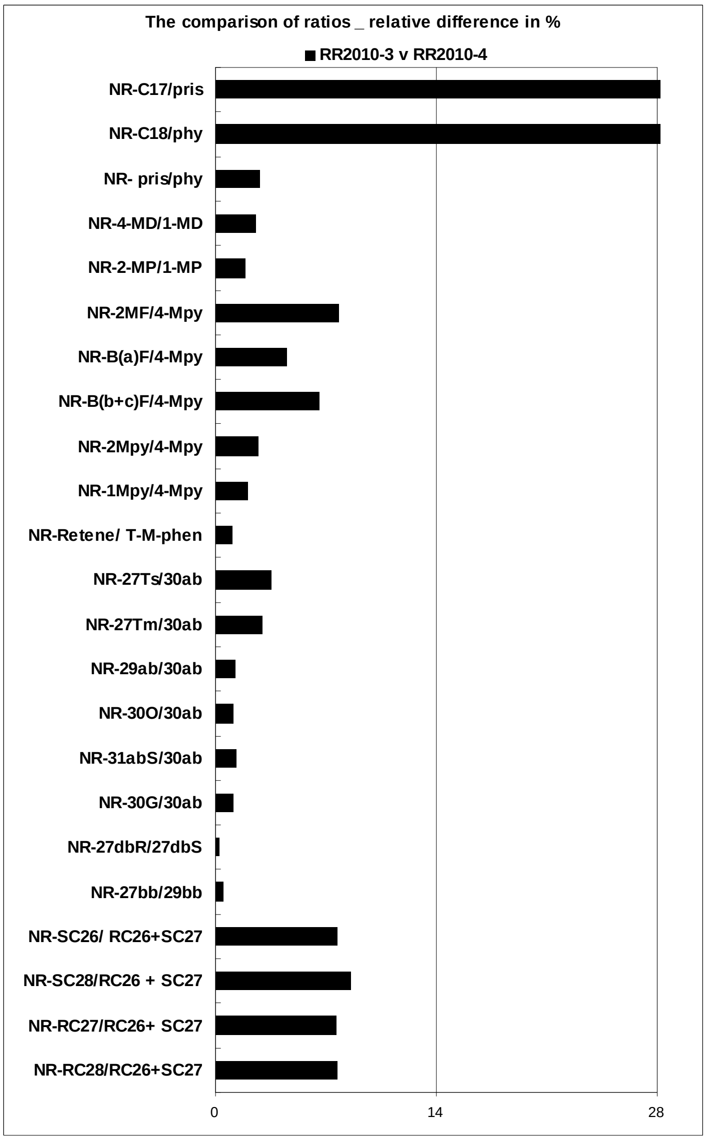
Fig. 27. Comparison of the RR2010-2 andRR2010-4: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The PW-plots show a similar pattern of RR2010-2 relative to RR2010-4. It can also be seen from the ratio comparison table and graph (Right side Fig. 27), that all ratios, except C17/pristane, are below the critical difference of 14%. The higher % of pristane and phytane in the MS-PW-plots of Fig 27 (around a ret time of 25 min.) is caused by some biodegradation of the alkanes. The difference is however small.

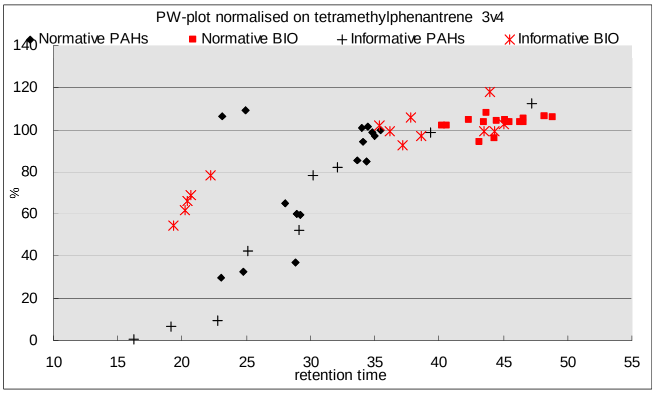
Conclusion: Positive Match

5.4.3 RR2010-3 vs RR2010-4

Ratio comparison graph:



PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)

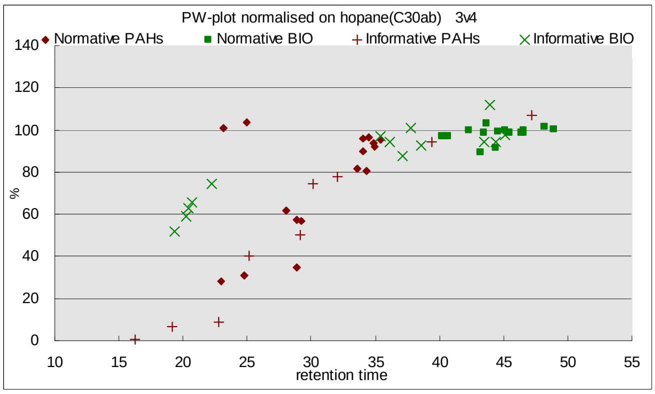


Fig. 28 Comparison of the RR2010-3 andRR2010-4: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The MS-PW plots illustrate that RR2010-3 is more weathered than RR2010-2 and RR2010-4. The change of n-C17/pristane and the n-C18/phytane ratios between RR2010-3 and RR2010-4 indicates biodegradation. Biodegradation primarily removes straight-chain hydrocarbons, and in later stages the branched saturated hydrocarbons. Saturated cyclic hydrocarbons are more resistant to biodegradation. Important biodegradation indicators are the isoprenoids and the effect of eventual microbial degradation can then be quantified by the relative loss of n-C17 and n-C18 compared to the less biodegradable pristane and phytane. In the

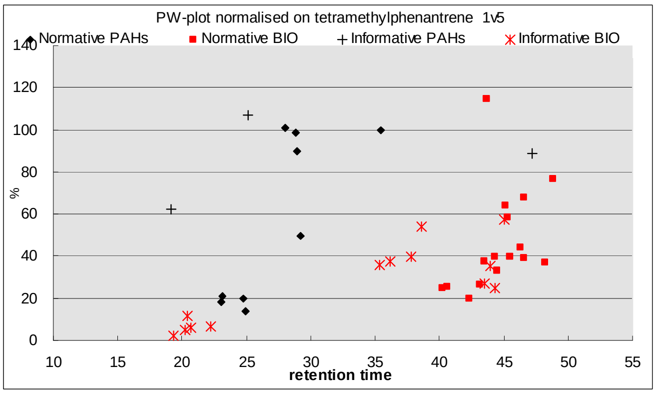
MS-PW-plots it is also very well visible that the sesquiterpanes (between ret. times of 20 tot 24 min.) are resistant against biodegradation, but not to evaporation.

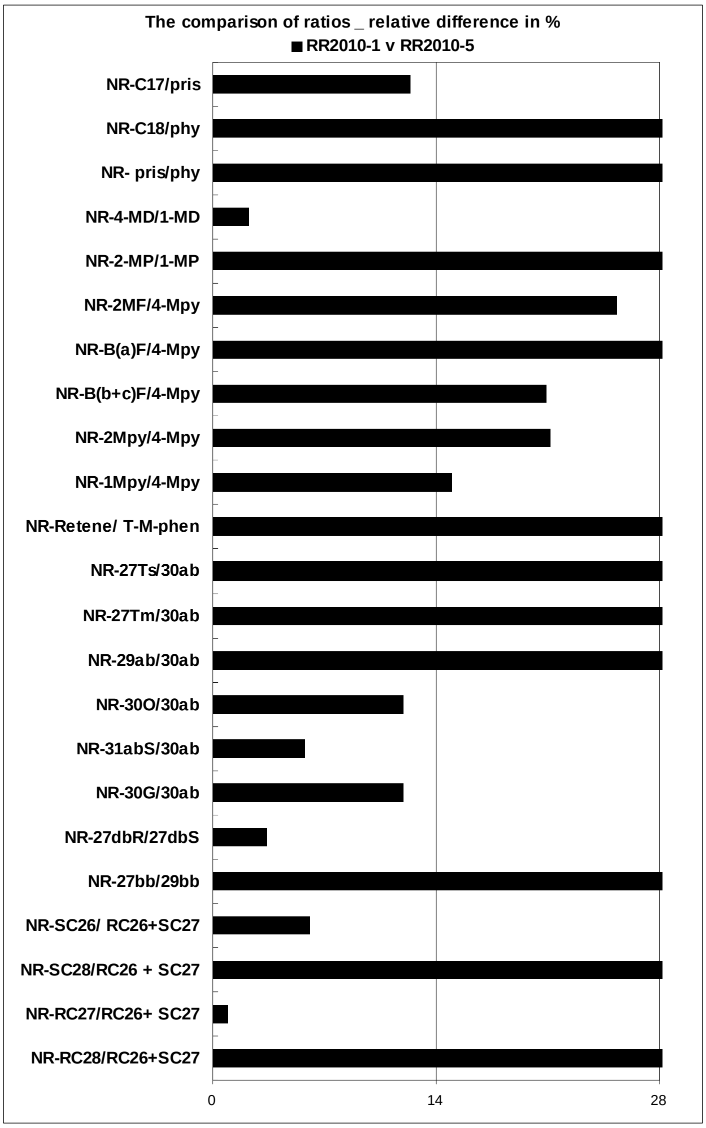
Conclusion: Positive Match

5.4.4 RR2010-1 vs RR2010-5

Ratio comparison graph:

PW-Plot normalized to tetramethylphenantrene





PW-Plot normalized to hopane(C30αβ)

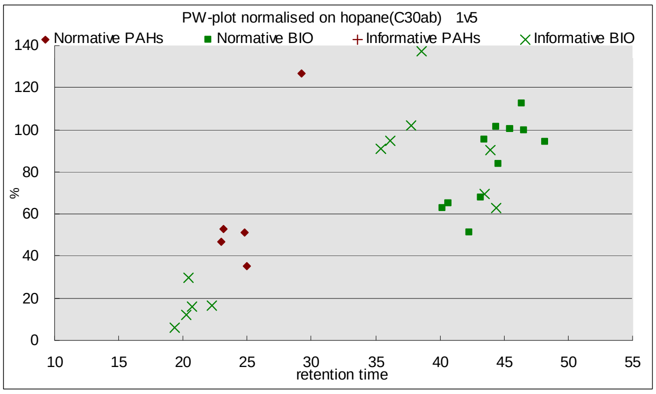


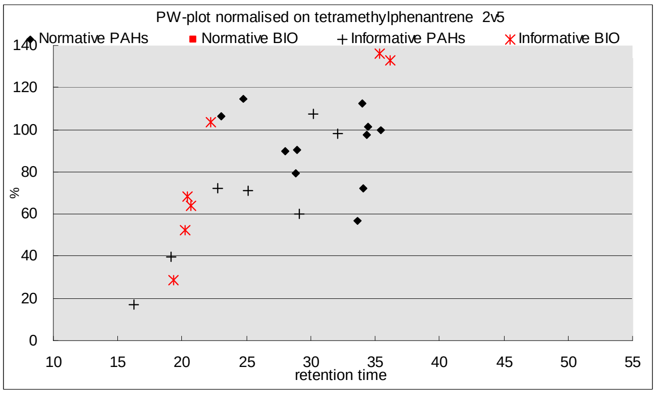
Fig. 29. Comparison of the RR2010-1 andRR2010-5: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The results confirm that these two samples are from different sources.

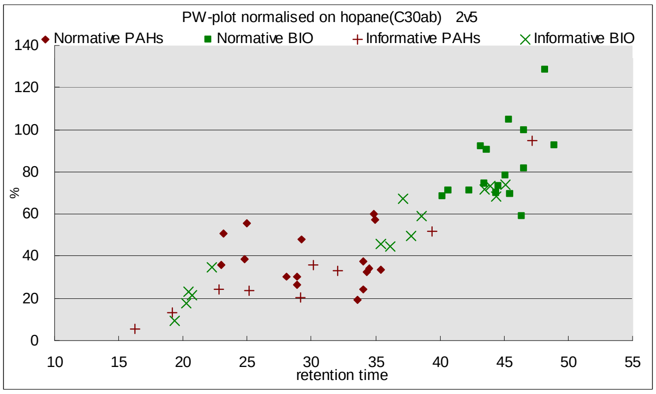
Conclusion: Non-Match

5.4.5 RR2010-2 vs RR2010-5

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

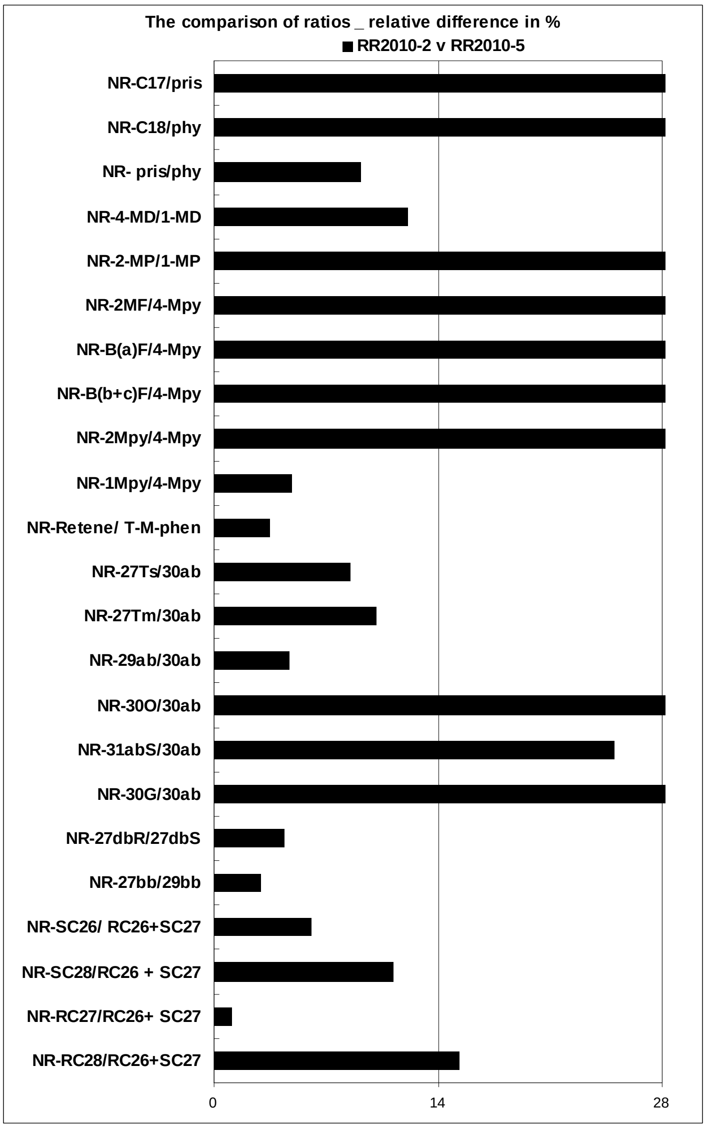


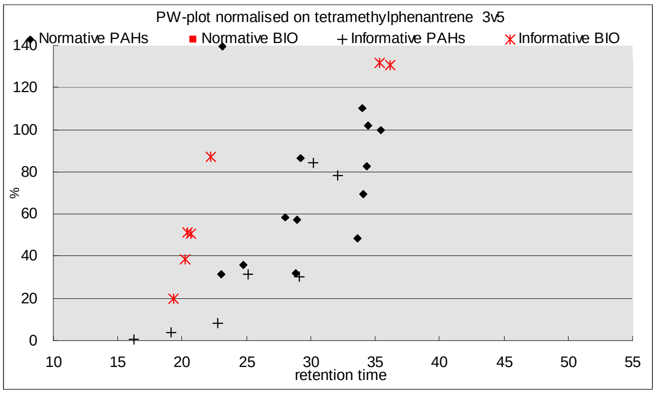
Fig. 30. Comparison of the RR2010-2 andRR2010-5: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The results confirm that these two samples are from different sources.

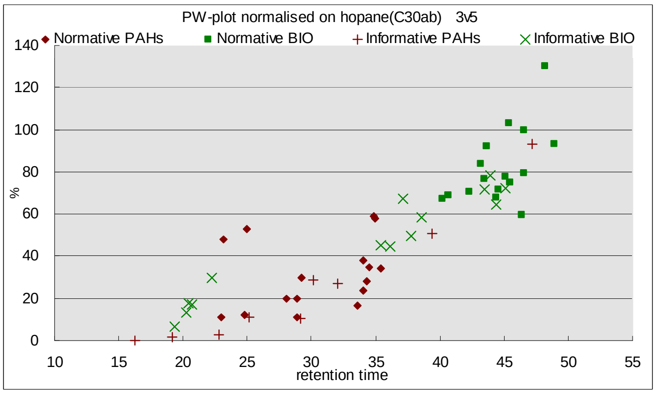
Conclusion: Non-Match

5.4.6 RR2010-3 vs RR2010-5

PW-Plot normalized to tetramethylphenantrene



PW-Plot normalized to hopane(C30αβ)



Ratio comparison graph:

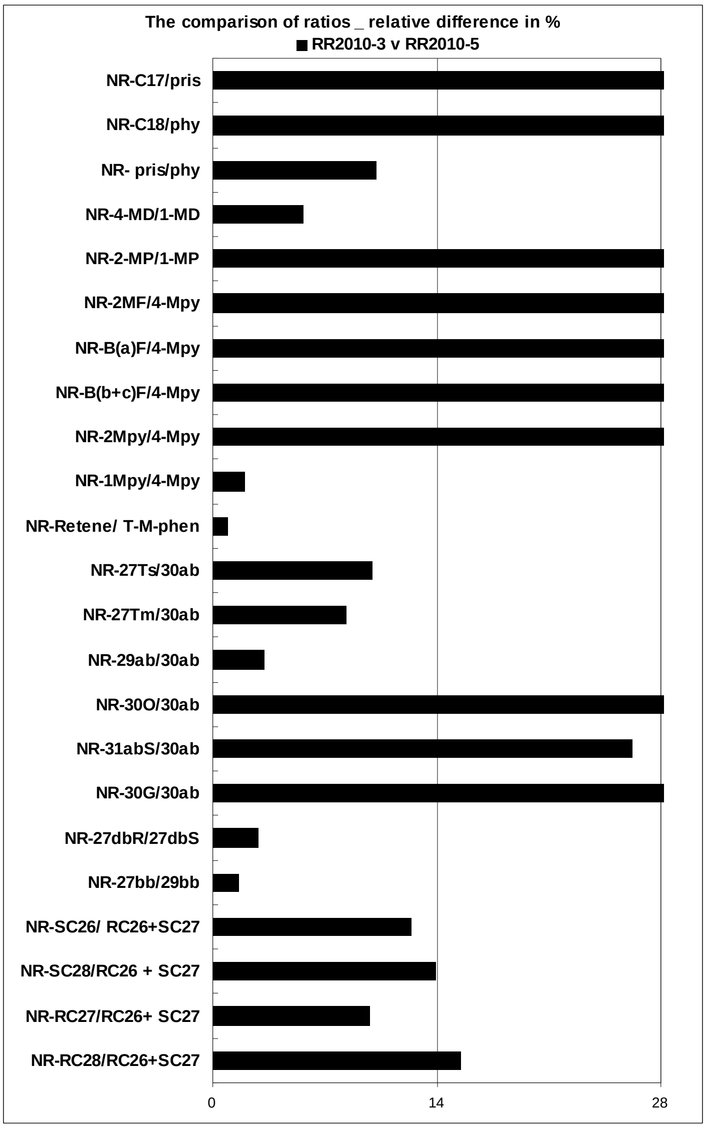


Fig. 31. Comparison of the RR2010-3 andRR2010-5: Normative ratios and MS-PW plot normalized to hopane / tetramethylphenantrene.

Discussion: The results confirm that these two samples are from different sources.

Conclusion: Non-Match

6 Conclusions

6.1 Oil type

In this Round Robin Test, identification of the oil type has been an important task. Although the CEN-TR 15522-2 gives a lot of information about HFO, it is clear from Round Robin sample 1 that the information doesn’t cover all types of HFO around the world. It can be concluded that:

- “methylanthracene has increased significantly” is still a valuable property of HFO
- that the methylphenantrene pattern can easily be affected by weathering and
- that the absence of retene is not valid for HFO found in the Bohai Sea area.

The application of a high temperature analysis has shown to give valuable extra information in the ability to differentiate between crude oil and an oil mixture of different oil products like HFO.

6.2 Comparison between the spill oil and source oil

Among all the spill oils, sample 1 and sample 5 are quite different from sample 4, all the participants got the right conclusion.

Sample 2 and sample 3 were from the same source, sample 4. Sample 2 was suffered from evaporation and slight biodegradation and sample 3 was suffered from evaporation, strong biodegradation and some waterwashing(in the stimulate device). All these kinds of weathering could be observed in the original chromatograms and PW-plots. So, a “Positive Match” could be got between sample 2, sample 3, and sample 4. As for spill samples with heavy biodegradation, a “Probable Match” can also be accepted, especially lack of environmental information which could affect weathering.

As an integral part of the CEN-methodology, MS-PW-plots can be used as a confirmation that differences between spill and source samples are caused by weathering effects. Such a confirmation is needed in order to come to the conclusion of a “positive match” despite those differences. But in order to explain those differences “unequivocally”, every deviation from the 100%-line has to be explained separately by taking into account the different processes of weathering, such as evaporation, bacterial degradation, dissolution and photo-oxidation.

7 Bibliography

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